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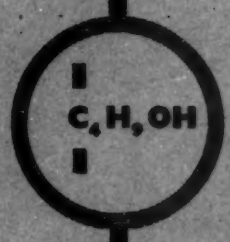

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20°/20°C : 0.808-0.812.
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THE INVERSION TEMPERATURE OF GASEOUS THERMAL DIFFUSION FACTORS

by **E. KYLE and C. J. G. RAW**

OPSOMMING

Die verandering van teken van die hittediffusie faktor teen 'n spesiale „omkeringstemperatuur" is teoreties bespreek. 'n Uitbreiding van die algemene kinetiese teorie van gasse toon aan dat dit moontlik is om die omkeringstemperatuur deur middel van die temperatuurafhanklikheid van die gewone (konsentrasie) diffusie koeffisient te bepaal.

SUMMARY

The change of sign of the gaseous thermal diffusion factor at a particular "inversion temperature" is discussed theoretically. An extension of the general kinetic theory of gases shows that it is possible to determine the inversion temperature from the temperature dependence of the ordinary (concentration) diffusion coefficient.

The thermal diffusion factor, α, of a binary mixture of gases, including isotopic mixtures, depends quite strongly on the temperature, but is almost independent of the relative proportions of the two gases. It is defined[1] by the relation:

$$\alpha = k_T / x_1 x_2$$

where x_1 and x_2 are the mole fractions of the two species, and k_T is the thermal diffusion ratio which occurs in the Chapman-Enskog equation of diffusion. For a binary gas mixture in a steady state across which a temperature gradient exists, this diffusion equation reduces to:

$$\text{grad } x_1 = -\frac{k_T}{T} \text{ grad } T$$

where T is the absolute temperature. On integration, this equation becomes

$$x_1 - x^1_1 = k_T \ln(T^1/T)$$

if k_T is treated as a constant. In this equation x_1 is the concentration of one species at temperature T, and x^1_1 is the concentration at T^1. The quantity $x_1 - x^1_1$ is termed the separation, and is what is usually measured in thermal diffusion experiments. The thermal diffusion ratio, k_T, depends in a complex fashion on the masses and diameters of the two species of molecule, and on the nature of the intermolecular forces, but shows a strong dependence on composition through the factor $x_1 x_2$. It is this which makes it useful to introduce the related quantity, α, the thermal diffusion factor, as defined above.

Empirically, a fair representation of the temperature dependence of α is afforded by the relation[2]:

$$\alpha = \alpha_0 (1 - A/T) \quad .. \quad .. \quad .. \quad .. \quad (1)$$

where α_0 is the limiting value of the thermal diffusion factor at high temperatures,

A is a constant, and T is the absolute temperature at which α is measured, i.e.

$$T=\frac{T_1T_2}{T_1-T_2}\ \ln T_1/T_2$$

where the two bulbs of the usual form of thermal diffusion apparatus are at temperatures T_1 and T_2 ($T_1>T_2$). The equation (1) represents fairly well the experimental variation of α with temperature, and also the predicted variation for the Lennard-Jones (12, 6) form[3] of the intermolecular potential.

At a certain particular temperature, T_0—usually referred to as the "inversion temperature"—the thermal diffusion factor may undergo a change in sign. At this inversion temperature, from (1),

$$(1-A/T_0)=0$$

so that the constant A may be interpreted as the temperature at which α changes sign. If the temperature dependence of α can be expressed in the form assumed in equation (1), then T_0 may be calculated from a knowledge of α_0 and α at some lower temperature, T:

$$T_0=T\left(\frac{\alpha_0-\alpha}{\alpha_0}\right) \quad .. \quad .. \quad .. \quad .. \quad (2)$$

According to Stier[4] and Holleran[5], the thermal separation ratio, R_T, is directly proportional to ln T for neon and argon. Thus,

$$R_T=a\ \ln(T/b)$$

where $R_T=\frac{\alpha(\text{exp})}{\alpha(\infty)}$ (α(exp)=the experimental thermal diffusion factor, $\alpha(\infty)$=the (constant) calculated value of α for rigid sphere molecules of the same mass and diameter as the molecules under consideration), and a and b are constants. For neon[1], a=0·25 and b=26·6, and for argon[1], a=0·25 and b=86·9.

At the inversion temperature, R_T (like α) will be zero, so that

$$\ln\ (T_0/b)=0 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (3)$$

It is thus possible to identify the inversion temperature with the constant b. For neon, then, T_0=26·6°K and for argon, T_0=86·9°K.

According to the rigorous kinetic theory of gases[3], the principal temperature dependence of the thermal diffusion factor is given by the term (6C*-5) where C* is a function of the reduced absolute temperature, kT/ϵ (ϵ=the maximum energy of attraction between two unlike molecules representative of the two species present, k=Boltzmann's constant). This combination of the kinetic theory "collision integrals," C*, has been computed and tabulated[3] for the fairly realistic Lennard-Jones (12,6) potential, and for the recently proposed[6,7] (exponential-six) model.

At the inversion temperature,

$$6C^*-5=0$$

For the Lennard-Jones (12,6) form of the intermolecular energy, C* has the value 0·8333 for kT/ϵ=0·404 and 0·933. Thus, two reversals of sign are predicted. Only one such change of sign has ever been observed, and that at the higher temperature. The Mason-Rice-Hirschfelder (exponential-six) model[6,7] also predicts two reversals of sign when the repulsion portion of the potential is not too "steep". The steepness of the repulsion for any form of intermolecular potential may be given in terms of the ratio σ/r_m where σ is the collision diameter (where the intermolecular potential

energy is zero) and r_m is the molecular separation where the intermolecular potential is equal to the maximum energy of attraction between molecules (i.e. r_m is the molecular separation at the potential energy minimum). For the (exp-six) potential, reversal of sign is only possible for relatively "soft" molecular collisions when $\sigma/r_m <$ 0·8942 (i.e. when the steepness parameter—denoted by α in the (exp-six) potential[6]—is less than 15). For "harder" collisions (involving a "steeper" repulsion), no reversal of sign is possible.

The fact that these fairly realistic molecular models predict two inversion temperatures while only one has ever been observed in practice, is probably due to the fact that, at the lower temperature, most substances have such small vapour pressures that they can hardly be considered to exist as gases at all, or, if they do exist as gases, quantum effects probably invalidate the classical calculations.

From the expression for C^* in terms of the collision integrals, and from a recursion relation between the collision integrals themselves, together with the kinetic theory expression for the ordinary (concentration) diffusion coefficient, D, Hirschfelder, Curtiss and Bird[3] have deduced a relationship between C^* and the temperature derivative of the diffusion coefficient at constant pressure,

$$C^* = \frac{3}{2} - \frac{5}{6}\left(\frac{\partial \ln D}{\partial \ln T}\right)_p$$

At the inversion temperature, $6C^* - 5 = 0$,

$$\text{thus, } \left(\frac{\partial \ln D}{\partial \ln T}\right)_p = 0{\cdot}8 \quad .. \quad .. \quad .. \quad .. \quad (4)$$

If we consider the plot of log D against log T at constant pressure, the inversion temperature is that temperature for which the slope is 0·8. Unfortunately, so little work has been done on the interdiffusion of gases over a range of temperatures (particularly low temperatures), that it is impossible, at the moment, to compare this result with experiment.

In addition to the ordinary "two-bulb" technique for determining thermal diffusion factors, Waldmann[8] has shown that it is also possible to obtain α from an experimental investigation of the reciprocal phenomenon—the diffusion thermo-effect (i.e. the instantaneous temperature gradient established in the process of ordinary diffusion). It is of some interest to note that it is possible, in Waldmann's experiments, to derive both the thermal diffusion factor and the ordinary diffusion factor. This should make possible a direct confirmation of equation (4) without the performance of separate experiments on diffusion and thermal diffusion.

The ordinary diffusion coefficient depends very strongly on the interaction of unlike molecules, and the thermal diffusion factor also does so, through the temperature dependence term, $(6C^* - 5)$, and hence it is not surprising that a relation of the form (4) exists.

The equations (2), (3) and (4) provide general and useful means of determining the inversion temperatures of gaseous thermal diffusion factors in different circumstances.

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THE INFLUENCE OF pH ON THE EXTRACTION OF ZINC, COBALT, NICKEL AND COPPER FROM TARTRATE SOLUTIONS USING DITHIZONE

by **D. J. EVE and A. STRASHEIM**

OPSOMMING

Die invloed van pH op ekstraksie, met chloroform-oplossings van ditisoon, van sink, kobalt, nikkel en koper, uit waterige tartraat oplossings, is ondersoek. Die eenvoudige verwantskap, voorgestel deur Koltoff en Sandell, is met sukses in die geval van nikkel en kobalt aangewend en die ewewigskonstant vir die ekstraksie van nikkel, kobalt en sink ditisoonate is bereken.

SUMMARY

The influence of pH on the extraction with chloroformic dithizone solutions of zinc, cobalt, nickel and copper from aqueous tartrate solutions, has been investigated. The simple expression proposed by Koltoff and Sandell has been shown to apply fairly well in the case of nickel and cobalt and equilibrium constants for the extraction of nickel, cobalt and zinc dithizonates have been calculated.

In recent years a number of publications have dealt with the application of dithizone extraction methods to the concentration of trace metals for spectrographic analysis. Dithizone extraction has also been applied extensively to the separation and concentration of metals for colorimetric and polarographic analysis. Except in the case of lead [1, 2] however, knowledge of the effect of pH on the efficiency of extraction is far from complete.

In the analysis of plant material it is common practice to add citrate or tartrate to the solution before it is neutralised in order to prevent the precipitation of metal hydroxides, especially iron and aluminium. Biefield and Partick [1] have shown that citrate solutions are unsuitable when lead is to be extracted and recommend the use of tartrate where a complexing agent is required. Unfortunately most of the work that has been carried out in connection with the influence of pH, deals with the extraction of metals from citrate solutions, and as the work of Biefield and Patrick shows, the nature of the complexing anions present can have a profound effect on the pH range of quantitative extraction. Furthermore, Yasumutsu Uzumasa and Isao Mujashito [2] have reported that tartrate and citrate interfere with the quantitative extraction of copper dithizonate by carbon tetrachloride.

A number of somewhat conflicting publications dealing with the extraction of zinc dithizonate have appeared [4, 5, 6], but in none of these is extraction from tartrate solution considered. Less work has been done on the extraction of cobalt. Marston and Dewey [7] have investigated the extraction of this element by a large excess of dithizone from the citrate and acetate solutions. They found a remarkable difference between carbon tetrachloride and chloroform as extractants.

Apparently little work has been done on the extraction of nickel with dithizone and no similar investigation of the extraction of copper from tartrate solutions has been published.

Fischer[8] has studied the pH ranges of stability of a number of metal dithizonates, but, as the results show, these have little relation to the pH ranges of complete extraction. Gorbach and Pohl[9] have recommended repeated extraction with dithizone over the pH range 7-9 for the extraction from plant material solutions of the trace metals zinc, copper, cobalt, nickel and lead, prior to their spectrochemical determination. As this procedure was found to be too slow, this investigation was primarily undertaken to investigate the possibility of extracting the elements in question at one optimum pH.

EXPERIMENTAL

During the course of this investigation two commercial brands of dithizone were used. In the first series of experiments a 46 *per cent.* pure product was used. Solutions prepared from this product were used for the preparation of the first series of pH-extraction curves for the individual metals. (These represent the smallest excess of dithizone). The second commercial product, obtained later, was shown to be 96 *per cent.* pure and this was used in all subsequent investigations.

8·2 *per cent.* (0·546 M) Tartaric acid solution (10 ml.)(corresponding to 10 *per cent.* ammonium tartrate) was run into a 200 ml. separatory funnel. Sufficient N ammonia solution was added to give approximately the desired pH (previously determined). A 10 p.p.m. solution (10 ml.) of the metal was then pipetted into the funnel and the mixture diluted to 100 ml. Dithizone solution (20 ml.) was added and the contents of the funnel were shaken vigorously for two minutes. The chloroform layer was separated and the pH of the aqueous phase determined.

In the estimation of cobalt, nickel and copper the chloroform layer was evaporated and the metal complexes destroyed by evaporation with nitric acid (5 ml.) containing a few drops of perchloric acid. The residue was dissolved in water containing a few drops of N HCl and, after diluting to 10 ml., the metal content was determined flame photometrically using a Beckman D.U. spectrophotometer with photomultiplier and flame attachments.

In the case of zinc, the excess dithizone in the chloroform phase was removed by extraction with ·04 *per cent.* sodium sulphide as described by Sandell[10] and the zinc content determined photometrically after dilution to 50 ml.

Nickel. Because of the metals studied, least is known about the extraction of nickel, a more thorough study was made of the effect of varying excesses of dithizone in the extraction of this metal than the others.

The results are shown in Figure 1.

Curve 1 shows the effect of variation in pH on the extraction of nickel using 20 ml. of ·0047 *per cent.* Dithizone (Dz), a 6·8 *per cent.* excess of the reagent.

Curve 2 shows the extraction with 20 ml. of ·0096 *per cent.* Dz (120 *per cent.* excess).

Curve 3 represents the result obtained when extractions were made with 14 ml. of ·0096 *per cent.* Dz to give a 54 *per cent.* excess.

Curve 4 shows the extraction with the same excess of reagent (54 *per cent.*), obtained by using 20 ml. of 0·007 *per cent.* Dz.

Cobalt. Figure 2 shows the results obtained for the extraction of cobalt. Extractions were made with two dithizone solutions, ·0096 *per cent.* and ·0047 *per cent.* giving excesses of reagent of 7·2 *per cent.* and 121 *per cent.* respectively.

Zinc and Copper. In Figure 3 the results obtained for the extraction of zinc and copper shown. In each case 20 ml. of ·0047 *per cent.* Dz were used for the extraction.

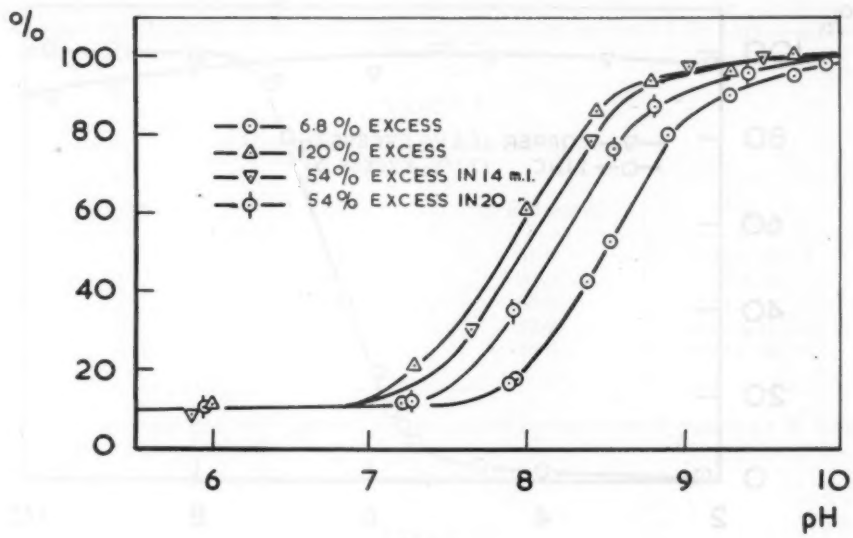

Fig. 1
pH—Extraction relationship for nickel.

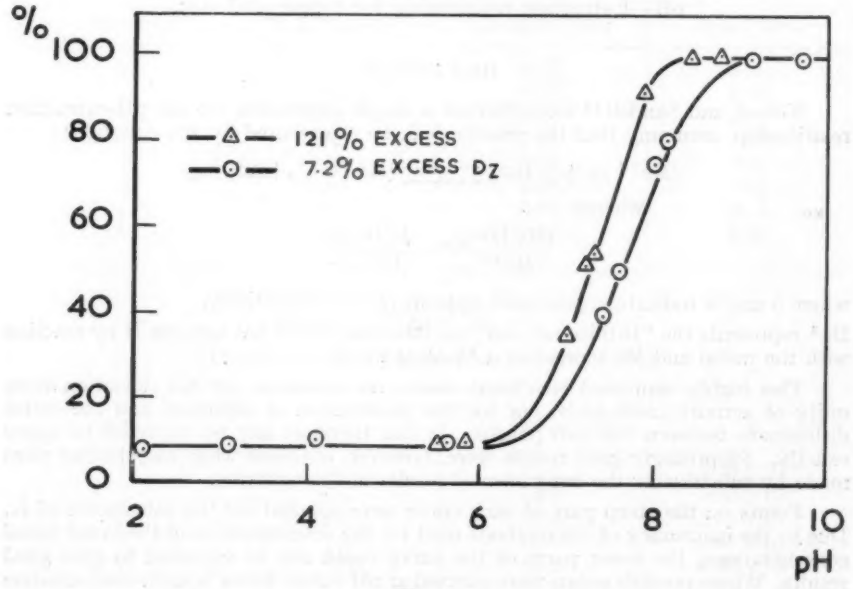

Fig. 2
pH—Extraction relationship for cobalt.

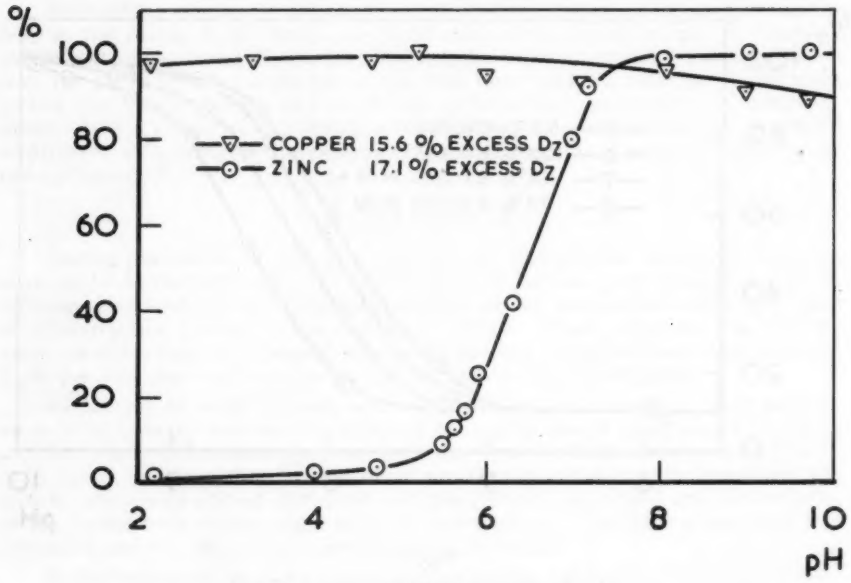

Fig. 3
pH—Extraction relationship for copper and zinc.

DISCUSSION

Koltoff and Sandell[11] have derived a simple expression for the pH-extraction relationship, assuming that the reaction ean be represented by the equation:

$$(Me^{2+})_w + (2\ Dz)_0 \rightleftharpoons (Me\ Dz^1_2)_0 + (2H^+)_w$$

whence

$$\frac{[Me\ Dz^1_2]_0}{[Me^{2+}]_w} = \frac{K[Dz]_0^2}{[H^+]_w^2}$$

where o and w indicate organic and aqueous phases respectively.

Dz^1 represents the "Dithizonate ion" i.e. dithizone which has lost one H by reaction with the metal and Me represents a bivalent metal.

This highly simplified treatment makes no allowance for the deviation from unity of activity coefficients, nor for the distribution of dithizone and the metal dithizonate between the two phases. It can therefore not be expected to apply exactly. Surprisingly good results were, however, obtained when calculations were made by substituting the experimental results in the equation.

Points on the steep part of each curve were selected for the calculation of K. Due to the inaccuracy of the methods used for the determination of the lower metal concentrations, the lower parts of the curve could not be expected to give good results. Where possible points were selected at pH values below 8, as in more alkaline solutions the position becomes somewhat complicated by the partial solution of the dithizone in the aqueous phase.[1]

Calculated values of K for the extraction of nickel, cobalt and zinc, are shown in Tables I, III and V while Tables II and IV illustrate the use of the expression for predicting the effect of varying the Dz concentration.

TABLE I

Calculation of K for Extraction of Nickel.

Curve	pH	% Extracted	K
1	8·5	51·0	$\cdot 55 \times 10^{-8}$
1	8·0	20·0	$\cdot 57 \times 10^{-8}$
2	8·0	60·0	$1 \cdot 01 \times 10^{-8}$
3	8·0	52·2	$1 \cdot 27 \times 10^{-8}$
4	8·0	40·5	$0 \cdot 91 \times 10^{-8}$

As the steep portion of curve 1 lies in the pH region above 8, values for K from this curve were neglected.

Mean K for curves 2, 3, 4, $= 1 \cdot 06 \times 10^{-8}$.

TABLE II

Calculation of points on the curves assuming that $K = 1 \cdot 06 \times 10^{-8}$

Curve	% Extracted	Calculated pH	pH found
1	70	8·72	8·79
1	40	8·19	8·34
2	70	8·21	8·17
2	40	7·76	7·68
3	70	8·29	8·27
3	40	7·88	7·81
4	70	8·37	8·45
4	40	7·96	8·00

TABLE III

Calculation of K for the Extraction of Cobalt

Curve	pH	% Extracted	K
1	8·0	71·5	$3 \cdot 40 \times 10^{-7}$
1	7·5	44·5	$3 \cdot 56 \times 10^{-7}$
2	8·0	96·5	$3 \cdot 11 \times 10^{-7}$
2	7·5	90·6	$3 \cdot 01 \times 10^{-7}$
2	7·0	35·0	$2 \cdot 26 \times 10^{-7}$

Mean K, $3 \cdot 07 \times 10^{-7}$

TABLE IV

Theoretical Calculation of Position of Curve 2 from Curve 1—Cobalt K (from curve 1), $3{\cdot}48\times10^{-7}$

% Extract	Calculated pH	pH Found
40	7·00	7·07
70	7·36	7·50

TABLE V

Calculation of K for the Extraction of Zinc

pH	% Extracted	K
7·0	79·5	$5{\cdot}38\times10^{-5}$
6·5	53·0	$5{\cdot}50\times10^{-5}$

Mean K, $5{\cdot}4\times10^{-5}$

From these results it has been concluded that at pH 9·5, using only a small excess of reagent, over 90 *per cent.* extraction was obtained in each case and therefore zinc, nickel, cobalt, copper and, from the results reported by Biefield and Patrick[1], lead may be quantitatively extracted from tartrate solutions at this pH. These observations led to the selection of pH 9·5 for all dithizone extractions for spectrographic analysis.

Comparison of the results obtained for zinc with those of Walkley[4] indicates that zinc may be extracted at a lower pH from tartrate than from citrate solution. This fact may prove valuable in the separation of zinc from other metals for colorimetric or polarographic analysis.

The results demonstrated in curves 3 and 4 of Fig. 1 for nickel indicate (with support from the theoretical calculation) that more efficient extraction may within certain limits be obtained by using the same weight of dithizone in a smaller volume of chloroform. These results also show the importance of stating all the experimental conditions when reporting work of this nature.

For nickel and cobalt, the expression derived by Koltoff and Sandell[11] may be used to predict the position of the pH extraction curves for any concentration of dithizone, provided K is known. Above pH 8, however, where dithizone becomes appreciably soluble in the aqueous phase, the relationship cannot be expected to apply.

The value of K as defined depends on the nature of the complexing anions in solution, as comparison with the observations of other workers shows. The possibility that the concentration of these anions may also affect the value of K should not be overlooked.

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THE KINETICS OF THE REACTION BETWEEN CUPRIC AND IODIDE IONS. PART I

by **D. M. KEMP and E. F. C. H. ROHWER**

OPSOMMING

Die snelheid van die reaksie tussen Cu^{++} en I^- is in 'n asynsuur-asetaat buffer-medium bepaal by verskillende konsentrasies van Cu^{++} en I^-, en van die suspensie van die neergeslane koper(I)-sout. Die reaksie begin in verdunde oplossings as 'n stadige, homogene reaksie wat na verskyning van die eerste sigbare neerslag na 'n vinniger, heterogeen-outokatalitiese reaksie verander. In die beperkte konsentrasiegebiede wat bestudeer is kan die reaksiesnelhede deur 'n formule:

$$-\frac{d[Cu^{++}]}{dt}=k[CuI][Cu^{++}]^x[I^-]^y \text{ weergegee word.}$$

In teenwoordigheid van oormaat KCNS is die reaksie, wat nou deur vaste CuCNS gekataliseer word, vinniger. In die formule vir die reaksiesnelhede neem die konsentrasie van die CuCNS suspensie die plek van CuI, en is die waardes van x en y kleiner as sonder KCNS. Met hierdie kinetiese gegewens word die verskynsels by die eindpunt in die jodometriese titrasie van koper bevredigend verklaar.

SUMMARY

The rates of the reaction between Cu^{++} and I^- in an acetic acid-acetate buffer medium have been determined for varying concentrations of the reactants and of the suspension of the cuprous salt precipitated. In dilute solutions the reaction begins as a slow, homogeneous reaction which merges on the first appearance of a precipitate into a more rapid, heterogeneous autocatalytic reaction. In the limited concentration ranges studied the rates can be represented by the formula:

$$-\frac{d[Cu^{++}]}{dt}=k[CuI][Cu^{++}]^x[I^-]^y.$$

In the presence of excess KCNS the reaction, now catalysed by solid CuCNS instead of CuI, is much faster. In the formula the concentration of the CuCNS suspension replaces CuI and the values of x and y are smaller than in the absence of KCNS. In terms of these kinetic data the effects observed near the equivalence point in the iodometric titration of copper are explained satisfactorily.

A study of the literature reveals that very little is known about the kinetics of the reaction between cupric and iodide ions. The early work of Traube[1] showed that the reaction is reversible and slow in dilute solutions. Later Oliveri-Mondala[2] found that the velocities of reaction between equivalent solutions of $CuSO_4$ and KI gave fairly good values for a trimolecular reaction. He noted, however, that precipitated CuI acted catalytically, thus complicating the reaction, but did not pursue the investigation further.

Preliminary experiments indicated the importance of kinetic effects in the iodometric determination of copper. This investigation was therefore started in order to extend the meagre experimental data available, especially for conditions similar to those obtaining near the equivalence point in the volumetric copper determination.

EXPERIMENTAL

In acid solution cupric and iodide ions in moderate concentrations—of the order 10^{-3} F with respect to Cu^{++} and 10^{-2} F with respect to I^-—react at a

conveniently measurable rate according to the equation:

$$2\,Cu^{++} + 5\,I^- = 2\,CuI\,(solid) + I_3^-$$

As the reaction is reversible it is essential, for the determination of the reaction rate, to suppress the reverse reaction effectively by removing one of the products. The only practical method for following the progress of the reaction in this concentration range was found to be manual addition of standard thiosulphate solution (approximately 0·01 N) to the reaction mixture at a rate just sufficient to repress the blue colour of the starch indicator. From the rate of addition of the thiosulphate solution, determined by noting with the aid of a stop watch the times at which the meniscus passed the various ml. markings on the burette, the rate at which Cu^{++} was being reduced could be calculated at any desired stage in the reaction. From the initial concentration of Cu^{++} and volume of the reaction mixture, together with the volume of thiosulphate solution added, the momentary concentration of Cu^{++} and of the CuI suspension produced could be calculated for any particular stage in the reaction. The concentration of potassium iodide, and of other salts if desired, was kept constant in the reaction mixture by adding them in suitable concentrations to the thiosulphate solution. These concentrations were calculated for each particular experiment so that the addition of these salts, simultaneously with the thiosulphate solution, would compensate precisely for the decrease of their concentration in the reaction mixture through reaction and/or dilution. This method of correcting for dilution effects could of course not be adopted for substances which reacted with thiosulphate, e.g. acids. When such correction became necessary, it was done by separate addition of these reagents in suitable concentrations at a rate proportional to the rate of addition of the thiosulphate solution.

No special apparatus or chemicals were required. The chemicals used were all of "analytical reagent" grade. Stock solutions were made with distilled water, with the customary precautions in the case of thiosulphate. The thiosulphate solutions of predetermined concentration and containing salts such as KI in known concentrations, were prepared from the stock solutions by suitable dilution with distilled, CO_2-free water just before use.

The reactions took place in a 400 ml. beaker immersed in a thermostat at 20°. In this beaker the reactants, previously brought to the temperature of the thermostat, were mixed at zero time and stirred mechanically at a uniform speed throughout the reaction.

In this series of experiments the initial volume of the reaction mixture was always 200 ml., contained 2 ml. freshly prepared 1 *per cent.* starch solution, and was $1{\cdot}21 \times 10^{-2}$ F with respect to sodium acetate and $1{\cdot}8 \times 10^{-1}$ F with respect to acetic acid giving a buffered solution of pH 3·6.

DISCUSSION

Curve 4 Fig. 1 represents a typical volume-time curve obtained in these experiments. The main obvious features of this curve indicate that initially, in the absence of solid cuprous iodide, the reaction is extremely slow. This "initial" reaction is succeeded, following the first appearance of a faint turbidity, by a period of rapidly increasing reaction rate. With progressing depletion of the cupric ions in the reaction mixture the reaction rate begins to fall off again, eventually approaching zero asymptotically. These sigmoid curves, typical of autocatalysed reactions, could readily be reproduced accurately except for one feature. Occasionally, under apparently identical conditions the length of the initial period of extremely slow reaction varied—sometimes quite markedly—from one experiment to the next.* By a slight

*The rate of the homogeneous reaction between Cu^{++} and I^- at low concentrations has been studied recently by Rohwer and Morkel. Dissolved oxygen has a remarkable accelerating effect on this reaction. Details of this investigation will appear in a later number.

horizontal shift, the remaining portion of the volume-time curves can, however, in such cases be superimposed satisfactorily, indicating that once a minimum amount of cuprous iodide has been formed, the reaction follows a strictly reproducible pattern. The shape and slopes of these curves were not affected by slight changes in the mode of addition of the thiosulphate solution. Experiments in which the thiosulphate solution was added at a rate which kept the starch indicator practically colourless throughout the reaction and those in which the thiosulphate was added at a rate which maintained a constant light but definitely blue hue, gave curves of identical shape. Hence it was concluded that the slopes of these curves are a reliable measure of the rate of the reaction between cupric and iodide ions under the given conditions.

Effects of the concentration of the cuprous iodide suspension. In Fig. 1 the curves characterise reactions in which the iodide ion concentration was kept constant at $2{\cdot}5\times10^{-2}$ F. The initial concentration of copper sulphate was varied as in Table I.

Fig. 1

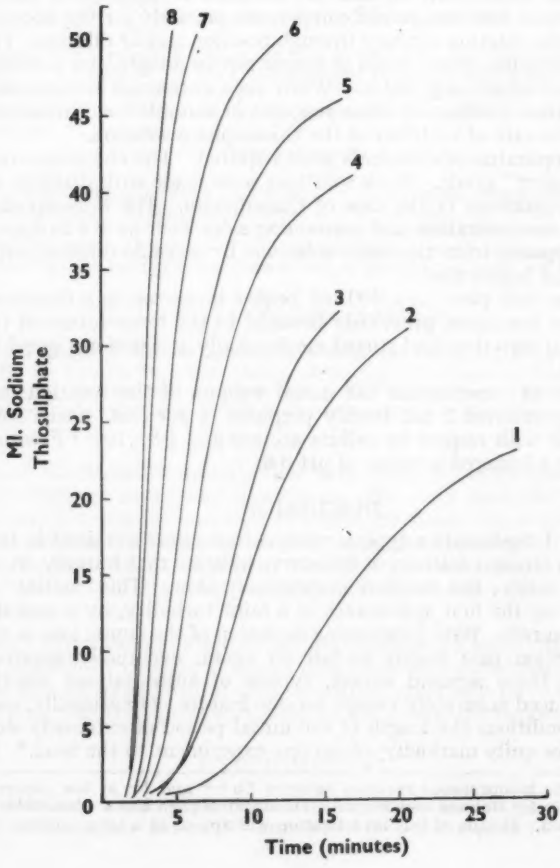


Table I

Curve	1	2	3	4	5	6	7	8	
[Cu++]	1·75	2·0	2·25	2·5	2·75	3·0	3·25	3·5	$\times 10^{-3}$ F

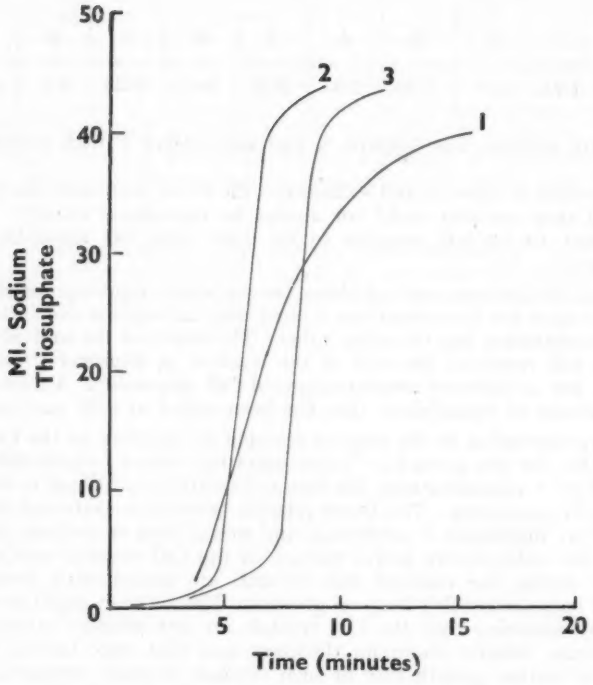
The thiosulphate solution was 0·00916 N and also 0·0342 F with respect to KI.

The intersection of curves 2 and 3 illustrates the effect mentioned above, namely that the initial slow reaction could not always be reproduced exactly. Curve 3, shifted somewhat to the left, parallel to the time axis, fits naturally into the sequence of curves.

At different heights on each of these curves which represent reactions with different initial cupric ion concentrations, a point may be found at which the momentary Cu^{++} concentration has the same value. The slopes of the individual curves at such points will represent the rate of the reaction at identical I^- and Cu^{++} concentrations, but at different concentrations of CuI suspension. A measure of the latter is the volume of thiosulphate that has been added at each particular point.

Graphic representation of the rates of reaction as functions of the CuI concentration shows that for any given Cu^{++} concentration, over a considerable range of both CuI and Cu^{++} concentrations, the rate is directly proportional to the concentration of the CuI suspension. This linear relation between the rate and the concentration of the CuI suspension is surprising, and would seem to indicate proportionality between the catalytically active surface of the CuI crystals and their total mass although during the reaction new crystals are continuously being formed while the older ones presumably keep on growing. This relation might be explained qualitatively by assuming that the CuI crystals are not efficient catalysts before reaching a certain, definite minimum thickness and that once having reached a certain size, the further growth rate of such crystals is small compared with the rate at which new crystals of the required size are produced during the course of the reaction. Qualitatively the latter assumption is supported by the appearance of the CuI precipitate. The former assumption is consistent with an interesting effect which is observed when a little silver nitrate is added to the potassium iodide solution just prior to the mixing with cupric sulphate: in Fig. 2, curve 1 is an ordinary volume-time curve for the reaction between Cu^{++} and I^-; curve 3 was obtained for an exactly similar reaction mixture except that 4 drops of a 0·2 N silver nitrate solution had first been added to the potassium iodide (2 drops $AgNO_3$ in the case of curve 2). The very fine suspension of the AgI formed caused a very marked extension of the initial period of extremely low reaction rate. On the other hand the heterogeneous reaction in the second phase, once started, was very much more rapid than without AgI. A tentative explanation of these phenomena is that in the presence of the large number of extremely fine AgI crystals the CuI produced during the slow, uncatalysed reaction deposits on the large, preformed, isomorphous AgI surface. Considerable time elapses before this large number of crystals has thus been covered by CuI and reached the required thickness for catalytic activity. Once this has eventually occurred, however, the active surface is very large compared with the total quantity of CuI precipitated, as the bulk of the interior of the crystals consist of preformed AgI. Hence the extraordinarily rapid heterogeneous reaction which follows. In the absence of preformed AgI crystals, with only a few crystal nuclei available, these few crystals will reach the necessary size sooner; but with the smaller active surface, the catalysed reaction though starting earlier, will proceed at a lower rate.

Fig. 2



These considerations do not, however, lead necessarily to a quantitative proportionality between the active surface and the total CuI present in normal reaction, but this may be accepted provisionally as an approximate, empirical relation under the experimental conditions described.

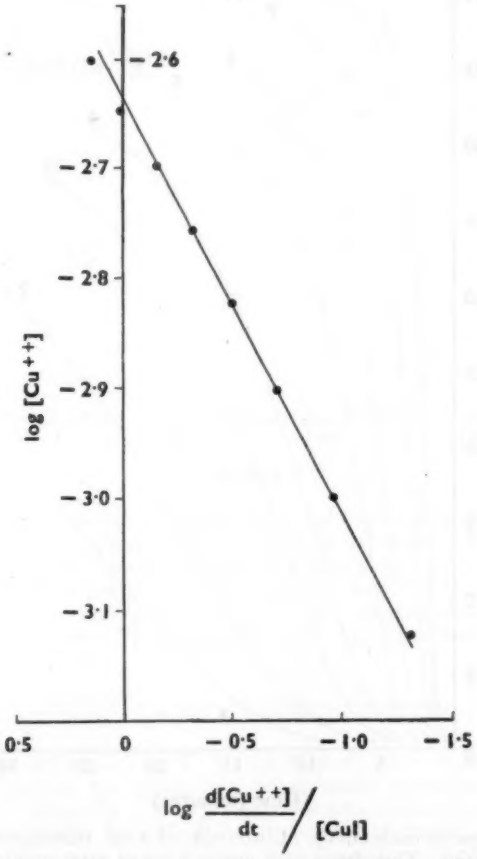
Effect of the concentration of cupric ions. In Fig. 1 the slopes of the various curves at points of intersection with a straight line parallel to the time axis, give rates at constant concentration of CuI which is represented by the volume of the thiosulphate added, and at different cupric ion concentrations for each curve. If such rates are plotted against the cupric ion concentration on a logarithmic scale a series of nearly straight and parallel lines is obtained, each line representing a particular value of the concentration of the CuI suspension. This indicates a power function for the effect of cupric ion concentration in the range studied. The same result is illustrated more effectively in the following way: by making use of the relation: rate $\propto$[CuI], the rates at a particular given cupric ion concentration but at different cuprous iodide concentrations determined from the experimental curves in the previous section, were all reduced to unit cuprous iodide concentration. The mean value of such reduced rates was determined for a range of cupric ion concentrations from $0{\cdot}75\times10^{-3}$ to $2{\cdot}5\times10^{-3}$ F. These mean corrected rates plotted against the cupric ion concentration on a logarithmic scale in Fig. 3 are very well represented by a straight line with a slope of 2·62. This gives as the partial rate law,

at constant iodide concentration ($2{\cdot}5\times10^{-2}$F) and in the given acetic acid-acetate buffer:

$$-\frac{d[Cu^{++}]}{dt}=k[CuI][Cu^{++}]^x$$

where x has the value 2·62.

Fig. 3



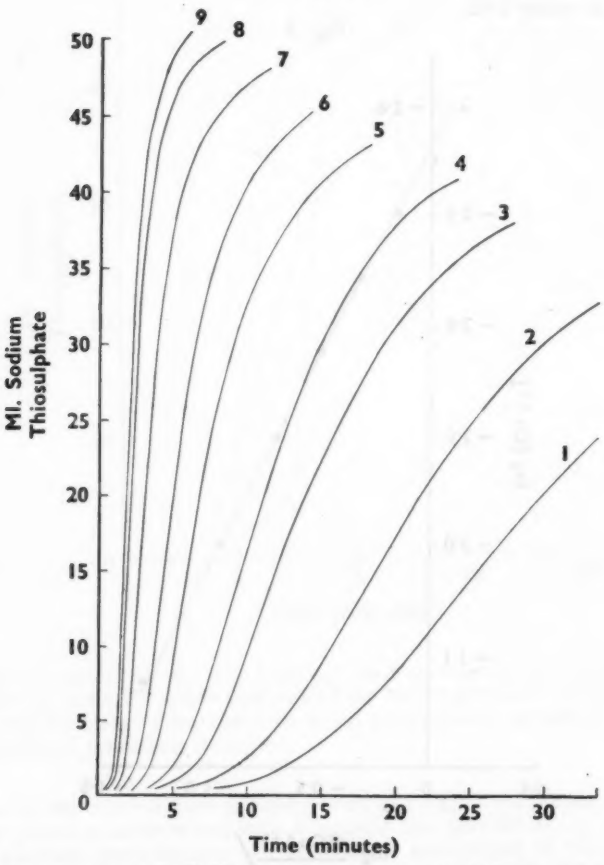
Effect of the concentration of iodide ions. Fig. 4 shows the volume-time curves for reactions, all with the same initial cupric sulphate concentration ($2{\cdot}75\times10^{-3}$ F). The potassium iodide concentration was systematically varied but kept constant during each individual reaction at values given in Table II.

Table II

Curve	1	2	3	4	5	6	7	8	9
[KI]	2·0	2·15	2·25	2·35	2·50	2·75	3·0	3·25	$3{\cdot}5\times10^{-2}$F

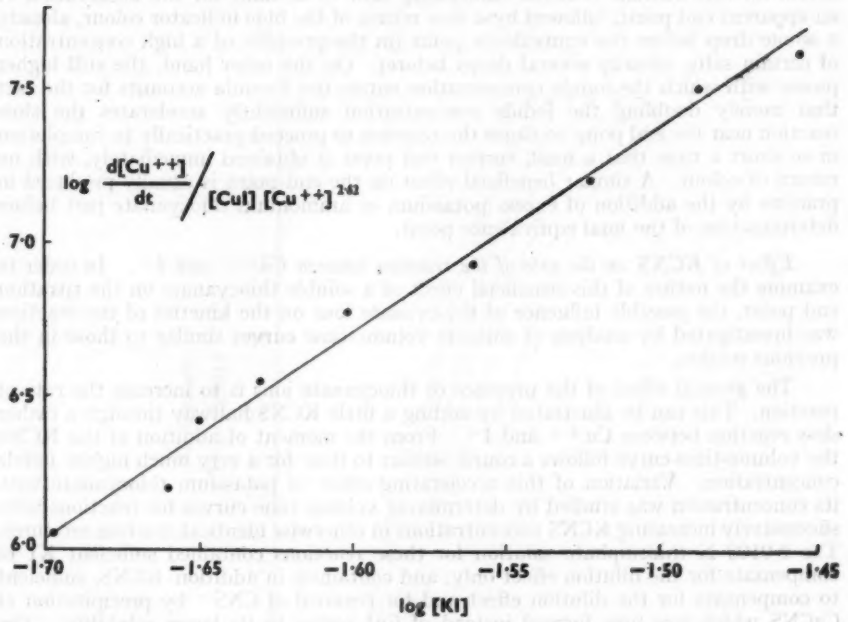
The thiosulphate solution was 0·00949 N, and for each individual reaction contained sufficient potassium iodide to keep its concentration in the reaction mixture constant at the given value.

Fig. 4



From the slope of each curve, at intervals of 5 ml. thiosulphate added, reaction rates were calculated. Thus from each curve a set of rates was obtained, all for the same potassium iodide concentration, but each for a different, known cupric ion and cuprous iodide concentration. Rates at corresponding points on different curves represent identical reaction mixtures except for the iodide concentration. Such rates, plotted against the iodide concentration on a logarithmic scale, gave a straight line, the lines for different values of cupric and cuprous iodide concentration being parallel. This indicates a power function for the effect of the iodide concentration. This result is again illustrated more effectively in the following way: the set of reaction rates determined for individual points on each particular curve was reduced to calculated rates at unit Cu^{++} and CuI concentration through division by the corresponding value of $[CuI][Cu^{++}]^{2 \cdot 62}$.

Fig. 5



The mean of these calculated reduced rates for each curve was plotted against the corresponding iodide-concentration on a logarithmic scale in Fig. 5. The points are fairly evenly distributed about a straight line with a slope of 6·2 and an intercept on the rate axis of 16·6. This gives as the empirical rate law for the heterogeneous reaction between cupric and iodide ions, in the concentration ranges studied ([KI], $2{\cdot}0\times10^{-2}$ to $3{\cdot}5\times10^{-2}$ F; [CuI], $2{\cdot}31\times10^{-4}$ to $17{\cdot}4\times10^{-4}$ F and [Cu++], $0{\cdot}5\times10^{-3}$ to $2{\cdot}5\times10^{-3}$ F):

$$-\frac{d[Cu^{++}]}{dt} = k_1[CuI]\cdot[Cu^{++}]^x\cdot[I^-]^y$$

where $k_1=10^{16\cdot6}$, $x=2{\cdot}62$ and $y=6{\cdot}2$. In this formula [Cu++] represents the total cupric salt concentration, no distinction being made between aquo- and other complexes of Cu++. Similarly [I−] represents the total iodide in solution, no correction being made for iodide ions possibly sequestered as cupric complexes. Such complex formation has a very marked effect as is shown by the pronounced influence of foreign salts on the reaction rate, which will be described in detail in a separate publication. In view of these facts it is not permissible to round off the values of the powers in the above expression to nearby simple figures for use in speculations on possible reaction mechanisms.

This empirical relation is, however, useful in the interpretation of the effects observed in the practical iodometric determination of copper. In accordance with the high power with which the cupric ion concentration appears in the formula, the reaction rate falls off rapidly as the equivalence point in the titration is approached. Calculation shows that in the presence of the customary amount of iodide, the re-

action on this account becomes sufficiently slow to account for the observation of an apparent end point, followed by a slow return of the blue indicator colour, already a whole drop before the equivalence point (in the presence of a high concentration of certain salts, already several drops before). On the other hand, the still higher power with which the iodide concentration enters the formula accounts for the fact that merely doubling the iodide concentration sufficiently accelerates the slow reaction near the end point to cause the reaction to proceed practically to completion in so short a time that a final, correct end point is obtained immediately, with no return of colour. A similar beneficial effect on the end point is usually produced in practice by the addition of excess potassium or ammonium thiocyanate just before determination of the final equivalence point.

Effect of KCNS on the rate of the reaction between Cu^{++} and I^-. In order to examine the nature of this beneficial effect of a soluble thiocyanate on the titration end point, the possible influence of thiocyanate ions on the kinetics of the reaction was investigated by analysis of suitable volume-time curves similar to those in the previous section.

The general effect of the presence of thiocyanate ions is to increase the rate of reaction. This can be illustrated by adding a little KCNS halfway through a rather slow reaction between Cu^{++} and I^-. From the moment of addition of the KCNS the volume-time curve follows a course similar to that for a very much higher iodide concentration. Variation of this accelerating effect of potassium thiocyanate with its concentration was studied by determining volume-time curves for reactions with successively increasing KCNS concentrations in otherwise identical reaction mixtures. The 0·0100 N thiosulphate solution for these reactions contained sufficient KI to compensate for the dilution effect only, and contained in addition KCNS, sufficient to compensate for the dilution effect and for removal of CNS^- by precipitation of CuCNS which was now formed instead of CuI owing to its lower solubility. The initial copper sulphate concentration was $2{\cdot}5\times10^{-3}$ F (about the mean of concentrations used in the previous sections). In order to keep the reaction rate in the conveniently measurable range, the potassium iodide concentration was chosen as low as $0{\cdot}75\times10^{-2}$ F, where in the absence of KCNS it had to be of the order $2{\cdot}5\times10^{-2}$ F.

Increasing the KCNS concentration affected the volume-time curves in two ways:

(1) the parts of the curves representing the rapid heterogeneous phase of the reaction became successively steeper,

(2) the periods of the initial slow reaction preceding the heterogeneous phase became successively shorter.

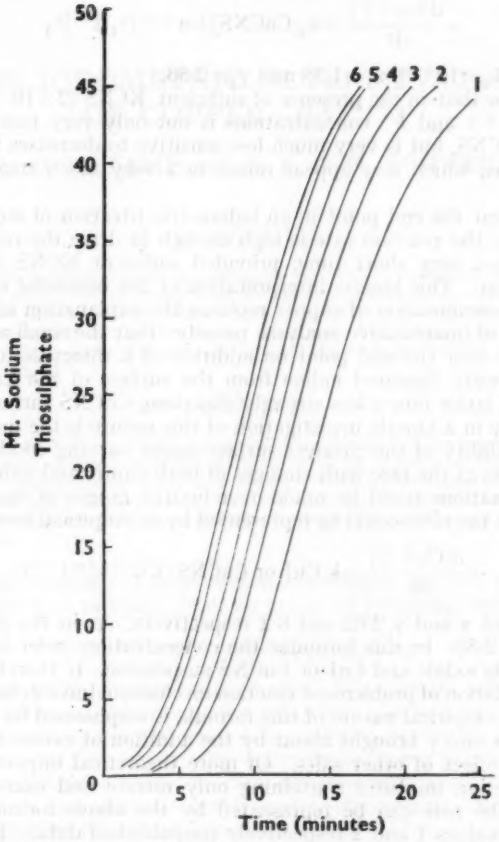
Eventually, however, a further increase in the KCNS concentration beyond the value 2×10^{-2} F caused no further increase in the rate of the heterogeneous reaction. Curves for KCNS concentrations in this region are shown in Fig. 6. The various KCNS concentrations are listed in Table III.

Table III

Curve	1	2	3	4	5	6	
[KCNS]	1·5	1·75	2·0	2·5	3·0	3·5	$\times10^{-2}$ F.

Curve 2 still shows a small but definite increase in the rate over that of the reaction represented by curve 1, but the curves from number 3 onwards are, within the limits of experimental error, perfectly parallel over the whole range representing

Fig. 6



the fast, heterogeneous part of the reaction. The period of the initial, slow reaction, however, continues to decrease with increasing concentration of KCNS even in this range.

These facts seem to indicate that the increase in reaction rate caused by the addition of KCNS is due to the greater catalytic activity of the surface of cuprous thiocyanate than that of cuprous iodide; the maximum effect is presumably attained when the concentration of thiocyanate has reached a value sufficiently high to ensure that the precipitate formed consists practically exclusively of CuCNS.

Rate law for the reaction in presence of excess KCNS. The effects of variation of the concentrations of Cu^{++}, I^- and CuCNS suspension was determined in a series of experiments exactly similar to the corresponding experiments described in previous sections, except that in addition a constant concentration of KCNS (2×10^{-2} F) was maintained in all the reaction mixtures, and that a lower range of KI concentrations ($0{\cdot}65\times10^{-2}$ to $1{\cdot}375\times10^{-2}$ F instead of 2×10^{-2} to $3{\cdot}5\times10^{-2}$ F) was employed. Analysis of the volume-time curves gave results exactly similar to those

obtained without KCNS. The rates could again be represented satisfactorily by the equation:

$$-\frac{d[Cu^{++}]}{dt} = k_2[CuCNS][Cu^{++}]^{x_1}[I^-]^{y_1}$$

where, however, $k_2 = 10^{8 \cdot 74}$, $x_1 = 1 \cdot 38$ and $y_1 = 2 \cdot 56$.
These results show that in the presence of sufficient KCNS (2×10^{-2} F) the reaction rate at given Cu^{++} and I^- concentrations is not only very much higher than in the absence of KCNS, but is very much less sensitive to decreases in the Cu^{++} and I^- concentrations, which now appear raised to a very much smaller power in the rate law.

Thus even near the end point in an iodometric titration of copper in moderate KI concentration, the reaction rate is high enough to drive the reaction practically to completion in a very short time, provided sufficient KCNS (i.e. solid CuCNS catalyst) is present. This kinetic interpretation of the beneficial effect of KCNS in the volumetric determination of copper replaces the explanation at present given in many text books of quantitative analysis, namely "that the small additional amount of iodide set free near the end point on addition of a thiocyanate, is produced by desorption of already liberated iodine from the surface of the CuI precipitate by conversion of the latter into a less strongly absorbing CuCNS surface."

One difficulty in a kinetic investigation of this nature is the uncertainty regarding the reproducibility of the catalyst surface under varying conditions. Owing to the great variation of the rate with changes of both cupric and iodide concentration, the rate determinations could be made over limited ranges of concentrations only. Over these ranges the rates could be represented by an empirical formulae of the type:

$$-\frac{d[Cu^{++}]}{dt} = k[CuI \text{ or } CuCNS][Cu^{++}]^x[I^-]^y$$

with the values of x and y 2·62 and 6·2 respectively, or, in the presence of excess KCNS, 1·38 and 2·56. In this formulae the concentrations refer to the total soluble cupric salt, soluble iodide and CuI or CuCNS suspension. It therefore does not lend itself to the elucidation of problems of reaction mechanism but can find useful practical application. The empirical nature of this formula is emphasised by the large changes in the values of x and y brought about by the addition of excess KCNS and by the strong retarding effect of other salts. Of more theoretical importance may be the fact that in reaction mixtures containing only nitrate and excess thiocyanate as foreign anions, the rate can be represented by the above formula with x and y approaching the values 1 and 2 respectively (unpublished data). In such a medium the reaction rate is furthermore much higher and is not affected by variation in nitrate concentrations in the range 0 to 0·2 F.

One of us (D.M.K.) is indebted to African Explosives and Chemical Industries Limited for a fellowship which made this research work possible. The experimental results cited in this paper are taken from the doctoral thesis by D. M. Kemp, University of Stellenbosch, 1954.

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THE IODOMETRIC DETERMINATION OF COPPER. PART I

by D. M. KEMP and E. F. C. H. ROHWER

OPSOMMING

Die resultate van die eksperimentele ondersoek van die skrywers oor die kinetiek van die reaksie tussen Cu^{++} en I^- ione is toegepas op die jodometriese bepaling van koper. 'n Titrasiemetode is ontwerp en uitgetoets wat sekere voordele het vergeleke met die bestaande metode, veral weens die geringer kaliumjodied-verbruik. Byvoeging van sirkoonchloried word aanbeveel i.p.v. die tans gebruiklike sorgvuldige pH-kontrole om die nadelige invloed van arsenate in die koperbepaling uit te skakel.

SUMMARY

The results of the authors' experimental study of the kinetics of the reaction between Cu^{++} and I^- ions are applied to the iodometric determination of copper. A titration procedure is developed and tested which offers certain advantages over the method used at present, especially in the lower potassium iodide consumption. Addition of zirconium chloride, instead of the careful pH control employed at present, is advocated to eliminate the interference of arsenates in the copper determination.

The well-known iodometric determination of copper depends on the liberation of an equivalent amount of iodine from an excess of potassium iodide according to the equation:

$$2\,Cu^{++} + 5\,I^- = 2\,CuI\ (solid) + I_3^- \quad .. \quad .. \quad .. \quad (1)$$

the liberated iodine being titrated with standard thiosulphate solution. Since the work of Foote and Vance[1] this volumetric procedure has become a method of high accuracy, a permanent correct end point being assured by the addition of 2 to 3 g. potassium thiocyanate just before the equivalence point is reached. Recently Hammock and Swift[2] have made an extensive re-examination of the conditions under which the titration yields accurate results. In essentials their work has left the method suggested by Foote and Vance unchanged.

One disadvantage of this method is the rather large quantity (2·5 to 3 g.) of the expensive potassium iodide required per titration. It is not surprising, therefore, that as early as 1917 Bruhns[3, 4, 5, 6, 7], in a series of publications described attempts to effect a saving of potassium iodide by substituting a soluble thiocyanate for the iodide in one of its functions, namely in its role as precipitating agent (equation 3) for the cuprous ions formed in the reduction of cupric ions by iodide:

$$2\,Cu^{++} + 3\,I^- = 2\,Cu^+ + I_3^- \quad .. \quad .. \quad .. \quad (2)$$

$$2\,Cu^+ + 2\,I^- = CuI\ (solid) \quad .. \quad .. \quad .. \quad (3)$$

$$\text{or } 2\,Cu^+ + 2\,CNS^- = 2\,CuCNS\ (solid) \quad .. \quad .. \quad .. \quad (3a)$$

$$I_3^- + 2\,S_2O_3^{=} = S_4O_6^{=} + 3\,I^- \quad .. \quad .. \quad .. \quad (4)$$

To accomplish this, Bruhns added potassium thiocyanate together with the potassium iodide at the beginning of the titration. Owing to its smaller solubility ($S_{CuCNS} = 4 \times 10^{-14}$, $S_{CuI} = 1{\cdot}1 \times 10^{-12}$)[8] only CuCNS should then be precipitated, so that the overall reaction could be represented by the equation:

$$2\,Cu^{++} + 2\,S_2O_3^{=} + 2\,CNS^- = 2\,CuCNS\ (solid) + S_4O_6^{=} \quad .. \quad (5)$$

with the iodine now acting only as, firstly, a potential mediator in the reduction of cupric ions by thiosulphate according to equations 2 and 4, and secondly, together with starch, as an indicator of the end point. In the ideal case it should then be possible to reduce the quantity of iodide required per titration to a very small amount. These attempts did not meet with the desired success; low results were obtained.

This effect was ascribed by Bruhns[9] and in a more extensive study by Kruger and Tschirch[10], mainly to partial irreversible oxidation of thiocyanate by cupric ions to HCN and sulphuric acid, and also to other products:

$$6\,Cu^{++} + 7\,CNS^{-} + 4\,H_2O = 6\,CuCNS + HCN + SO_4^{=} + 7\,H^{+} \quad .. \quad (6)$$

In many cases small amounts of "black $Cu(CNS)_2$" were said to be occluded in the CuCNS crystals, which darkened the suspension, thus obscuring the starch-iodide end point. These findings were again confirmed by Hammock and Swift[2] in their more recent work.

The difficult supply position during the last years of the Second World War prompted re-investigation of the possibility of partial substitution of potassium thiocyanate for potassium iodide in the copper determination. Preliminary experiments on the kinetics of the reaction between cupric and iodide ions indicated a method which proved successful, and which has since been used in the author's laboratories with considerable saving of materials. The more detailed study by Kemp and Rohwer[11] of the reaction kinetics involved, provided a sound theoretical basis for the procedure. It was thereupon critically re-examined and its limitations were determined more precisely.

EXPERIMENTAL

The titration was carried out by the "double-burette method." From one burette the 0·1 to 0·05 N copper sulphate solution, whose concentration was to be determined, was run into acidified potassium iodide in the titration flask in small portions (3 to 10 ml.) at a time. The liberated iodine was almost completely reduced after each addition by titration with the standard thiosulphate from the second burette. These alternate additions of the Cu^{++} and $S_2O_3^{=}$ solutions followed each other in rapid succession, no attempt whatsoever being made to approach the equivalence point closely at any stage. When approximately 10 ml. of the Cu^{++} solution had thus been delivered, 2 g. KCNS—usually as 20 ml. of a 10 *per cent.* solution—were added to the titration flask. The alternate addition of the two solutions from the burettes was continued, 2 ml. 1 *per cent.* starch-indicator solution being added when more than 20 ml. of each of the two solutions had been delivered. After this, accurate equivalence points were obtained.

In this way a number of duplicate titration results could be obtained in a very short time with only one filling of the burettes and with only one portion of KI and KCNS. Accidental overtitration could be rectified by addition of a few drops from the other burette. Normally, except at the equivalence point, Cu^{++} is kept in excess in the titration flask, as thiosulphate in excess in the acid solution tends to decompose. This decomposition is so slow in dilute solution, however, that a momentary accidental excess, even of several ml. of the thiosulphate solution was found to cause no noticeable error provided the position was immediately rectified by addition of cupric solution from the other burette. There was no uncertainty about the end point, as this was taken as that point giving the most marked colour change per drop of reagent added.

Titration ratio values obtained by this method, employing systematically decreasing quantities of potassium iodide, were compared with titration ratios for the same solutions, determined by a standard procedure[2].

Normax Volume Burettes (50 ml.), standardised by the U.S. National Bureau of Standards, were used. The chemicals used were all of "analytical reagent" grade. Stock solutions were prepared with distilled water, with the customary precautions in the case of sodium thiosulphate. Blank titrations were carried out on all materials used; in no case did the blank amount to more than 0·005 ml. of the thiosulphate solution. No corrections were therefore made.

RESULTS AND DISCUSSION

The titration ratios obtained by the standard procedure for the two sets of copper sulphate and sodium thiosulphate solutions used were:

$$\text{Solutions A, } \frac{\text{ml. } Na_2S_2O_3}{\text{ml. } CuSO_4}\text{: 0·9843 (mean of 8 titrations)}$$

$$\text{Solutions B, } \frac{\text{ml. } Na_2S_2O_3}{\text{ml. } CuSO_4}\text{: 1·0348 (mean of 16 titrations).}$$

The maximum deviation observed in individual titrations was 0·04 *per cent.* The individual determinations were evenly distributed over the period during which the solutions were employed. The deviations of individual determinations from the mean value showed no trend with progressing age of the solutions. No significant difference was observed when acetic acid was replaced by sulphuric acid and ammonium sulphate.

The details of a typical titration according to the proposed double burette method are given in Table I.

TABLE I

Titration flask contained 10 *per cent.* KI solution (10 ml.) $(NH_4)_2SO_4$ (12 g.) and 1N H_2SO_4 (10 ml.).

Burettes filled with solutions A

Burette readings in ml.		Titration ratio
Ml. $Na_2S_2O_3$	Ml. $CuSO_4$	$\frac{\text{Ml. } Na_2S_2O_3}{\text{Ml. } CuSO_4}$
ca. 8·5	*ca.* 10	
	20 ml. KCNS added	
ca. 14	*ca.* 15	
ca. 18·5	*ca.* 20	
ca. 23·5	*ca.* 25	
	5 ml. 1 *per cent.* starch added	
25·12	25·52	0·9843
25·70	26·12	0·9839
26·52	26·92	0·9851
29·62	30·11	0·9837
30·60	31·11	0·9836
33·50	34·04	0·9841
36·14	36·70	0·9847
39·60	40·20	0·9851
40·96	41·59	0·9848
41·73	42·40	0·9842
		Mean: 0·9844

The mean titration ratio agrees well with the mean standardisation value 0·9843. The individual readings obtained show a maximum deviation of only 1 in 1200 from the mean value, and show no trend in one direction as the volume increases. The colour at each end point changed sharply to an almost perfect white. Each of the end points thus represents a perfectly satisfactory titration, the deviations of individual readings being typical deviations due to the inherent inaccuracies of the volume measurements. These results show that, contrary to statements even in recent publications[2], it is permissible to add the thiocyanate early in the titration, provided certain conditions, which follow from the knowledge of the factors governing the kinetics of the reactions involved, are strictly adhered to.

The undesirable irreversible oxidation of thiocyanate by cupric ions leading to low titration results is a slow reaction. Its occurrence during the titration was eliminated, or reduced to negligible proportions, by ensuring that the thiocyanate was at no stage in contact with appreciable concentrations of Cu^{++} for any length of time. For this reason the cupric solution was added in small quantities at a time. Further, conditions were maintained which favoured the rapid reaction of these quantities of Cu^{++} in the desired reduction by iodide ions. The homogeneous reduction of Cu^{++} by I^- was slow in dilute solution. No thiocyanate was therefore added before a reasonable amount of solid CuI had been formed. Once this had occurred, addition of excess KCNS changed this precipitate—at least superficially—into the still more efficient catalyst CuCNS. The remaining cupric solution could then be added at the normal delivery rate from the burette, since it was reduced and precipitated as CuCNS practically as fast as it entered the solution, provided the iodide concentration was sufficiently high. If, as in this work, it is desired to reduce the amount of potassium iodide required per titration to as low a value as possible, cognisance has to be taken of the fact that by such addition of Cu^{++} a considerable amount of iodide may become temporarily tied up as I_3^-. In consequence the reaction, initially fast enough, may slow down sufficiently to enable the undesirable reaction to compete. For this reason the stepwise addition of the cupric solution was continued and the triiodide formed in each step reduced to iodide by titration with thiosulphate between successive additions. Thus the only major decrease in the I^- concentration during the course of the titration was due to the dilution effect.

In order to determine how far the quantity of potassium iodide may be safely reduced, a number of titrations were carried out with successively decreasing quantities of KI. The results are shown in Table II. The letters A and B in the first column refer to the set of copper sulphate and sodium thiosulphate solutions used. These results indicate that with amounts of potassium iodide as low as 1 g., individual titrations show no greater maximum deviations than were observed in the standard method using 3 g. Even with as little as 0·5 g. KI the maximum deviation observed was less than 1 in 1000, and, if no greater accuracy than this is required, this method can be used with confidence with this small amount of KI.

Table II

Experiment No.	Grams KI	Mean titration ratio	Deviation from standard value
A 9—1	3·0	0·9848	+0·05 per cent.
—2	3·0	0·9848	+0·05 „ „
—3	3·0	0·9848	+0·05 „ „
—4	3·0	0·9847	+0·04 „ „
A 11—	3·0	0·9843	0·00 „ „
B 17—	3·0	1·0351	+0·03 „ „
B 23—	3·0	1·0346	−0·02 „ „
B 18—1	2·5	1·0351	+0·03 „ „
—2	2·5	1·0351	+0·03 „ „
B 24—1	2·5	1·0345	−0·03 „ „
—2	2·5	1·0345	−0·03 „ „
B 19—1	2·0	1·0347	−0·01 „ „
—2	2·0	1·0347	−0·01 „ „
B 25—1	2·0	1·0343	−0·05 „ „
—2	2·0	1·0345	−0·03 „ „
A 12—	1·5	0·9841	−0·02 „ „
B 20—1	1·5	1·0347	−0·01 „ „
—2	1·5	1·0344	−0·04 „ „
B 26—1	1·5	1·0343	−0·05 „ „
—2	1·5	1·0343	−0·05 „ „
A 10—1	1·0	0·9843	0·00 „ „
—2	1·0	0·9844	+0·01 „ „
A 13—1	1·0	0·9843	0·00 „ „
—2	1·0	0·9842	−0·01 „ „
B 21—1	1·0	1·0349	+0·01 „ „
—2	1·0	1·0345	−0·03 „ „
B 27—	1·0	1·0344	−0·04 „ „
A 14—	0·75	0·9837	−0·06 „ „
A 15—	0·5	0·9835	−0·08 „ „
B 22—	0·5	1·0344	−0·04 „ „

In each of these titrations a total volume of about 40 ml. of the *ca.* 0·1N cupric sulphate (4 millimoles) was titrated, resulting in a final volume of about 100 ml. in the titration flask. If the thiocyanate is added before 10 ml. of the Cu^{++} solution have been added, less than one millimole of I^- will have become tied up as CuI. Starting with 1 g. KI (6 millimoles) this leaves at the final equivalence point an iodide concentration of more than 0·05 F. At this iodide concentration, in the presence of CuCNS catalyst, the reaction is so fast that a final, correct end point is obtained immediately and irreversible oxidation of thiosulphate by Cu^{++} does not take place.

With only 0·5 g. KI (3 millimoles) the concentrations approach critical values. With one millimole I^- tied up as CuI, the iodide concentration at the final equivalence point is of the order 0·02 F, a value at which the reaction rate drops sufficiently to give an apparent end point resulting in a titration error which may be as high as one part per 1000. If in this titration the Cu^{++} solution is added in portions of more than 5 ml. at a time, so much iodide is temporarily tied up as I_3^- that the rate of reduction of Cu^{++} by I^- drops sufficiently to allow the undesired irreversible reaction with thiocyanate to compete, resulting in a darkening of the suspension.

With this small amount of iodide it is quite impossible to carry out the titration by the standard method, since here 4 millimoles of I^- are necessary for the precipitation of CuI alone. With 1 g. of KI, the position at the end point would be similar to that in the above double burette titration using only 0·5 g. KI.

Considerable saving of potassium iodide can thus be achieved by using this form of double burette titration in the iodometric copper determination. This method is especially useful in teaching institutions in that it provides the possibility of repeated equivalence point determinations with but one burette filling and with only one small portion of potassium iodide. In this method the ideal of Bruhns, to carry out the reaction in such a way that the sole function of the iodide is to act as a potential mediator in the reduction of Cu^{++} by thiosulphate and, together with starch, as indicator of the end point, is realised, except for the part of the reaction at the beginning of the titration. The amount of KI required, though considerably reduced, can however not be decreased to extremely small values, since in order to act efficiently as potential mediator, the iodide concentration must be at least about 0·02 F.

As will be evident from the effect of complexing anions on the rate of reaction between Cu^{++} and I^- [11], the lowest concentrations of I^- would be required in nitrate or perchlorate media. Nitrate media are not recommended on account of the possibility of contamination with small quantities of lower oxides of nitrogen. Perchlorate media have already been employed successfully in the determination of copper in sulphide ores [12]. In the presence of certain interfering substances, such as Fe^{III} and As^V it has been necessary to employ higher concentrations of complexing salts in order to reduce the concentration of Fe^{III}, or to buffer the solution in the vicinity of pH 4 in order to eliminate oxidation of iodide by arsenate [13, 14, 15]. In such cases higher iodide concentrations are necessary, also in the double burette method. The details of the investigation of these problems will be published later, but one result with practical application can already be stated: the careful buffering in the presence of As^V can be avoided by the addition of 10 *per cent.* zirconium chloride solution (2·5 ml. for every 0·1 g. As^V present at the equivalence point). Instead of decreasing the oxidation potential of As^V by reducing the hydrogen ion concentration, the oxidation potential is here sufficiently reduced by precipitation of the very insoluble zirconium arsenate, even in 0·1 N sulphuric acid in the presence of excess ammonium sulphate.

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REACTIONS OF TERTIARY BUTYL HYPOCHLORITE. PART I. NUCLEAR CHLORINATION OF ANILIDES WITH A NOTE ON THE N-CHLORINATION OF CERTAIN AMIDES

by **S. S. ISRAELSTAM**

OPSOMMING

Tersiêre butiel hipochloriet is gebruik vir chlorinasie in die nukleus van anilide en vir die bereiding van N-chlooramide.

SUMMARY

Tertiary butyl hypochlorite is used for the nuclear chlorination of anilides and for the preparation of N-chloroamides.

The use of tertiary butyl hypochlorite as a chlorinating agent was first suggested by Clark[1] who pointed out its many advantages for this purpose. In recent years this reagent has become more prominent (Anbar and Ginsburg[2] have reviewed its use) and a study of its reactions in these laboratories was undertaken. This paper reports the use of tertiary butyl hypochlorite for the nuclear chlorination of anilides and the preparation of N-chloroamides. A subsequent paper deals with the N-chlorination of anilides.

Among the existing methods of preparing chloroanilides are treating an acetic acid solution of the anilide with bleaching powder[3, 4, 5], chlorine gas[6, 3], or sodium chlorate and hydrochloric acid[7]. Clark[1] reported the preparation of *p*-chloroacetanilide by using tertiary butyl hypochlorite but gave no details.

The method now reported consists in dissolving the anilide in a mixture of carbon tetrachloride and glacial acetic acid and adding an equimolecular quantity of tertiary butyl hypochlorite. Where the resulting chloroanilide is not very soluble in methanol, the latter or the latter mixed with acetic acid may be used as the solvent. By this method the chlorination of the following anilides was investigated: acetanilide, benzanilide, propionanilide, aceto-*p*-toluidide, aceto-*o*-toluidide, aceto-*p*-anisidide, aceto-*α*-naphthalide and aceto-*β*-napthalide. All excepting aceto-*p*-anisidide gave chloroanilides. In the case of the anisidide, either in methanol or carbon tetrachloride : acetic acid solution, the only product isolated was a small quantity of a crystalline compound which from its melting point, 180° (uncorr.) might have been the deacetylated compound, 2-chloro-4-aminophenol methyl ether. Acetanilide, benzanilide and propionanilide gave as the main product in each case the 4-chloro derivative.

These results are in accordance with the view of Anbar and Ginsburg[8] that nuclear chlorination usually takes place in polar media when using tertiary butyl hypochlorite. Unless the *para* position is blocked, chlorination takes place mainly in this position.

N-Chloramides were obtained by dissolving the amide in a mixture of carbon tetrachloride and glacial acetic acid and adding an equimolecular quantity of tertiary butyl hypochlorite. Acetamide and benzamide gave very good yields of N-chloroamides. *p*-Toluenesulphonamide in methanol solution yielded N-chloro-*p*-toluenesulphonamide. No nuclear chlorination occurred in the case of benzamide, which is in accordance with the fact that direct chlorination of the ring by means of chlorine has as yet not been reported.

That only N-chlorination of benzamide occurred may be due to the inactivation of the *ortho* and *para* hydrogen atoms by the amide group and the relatively higher activity of the amide hydrogen atom compared with that of the hydrogen atom *meta* to the amide group. A further study of the chlorination of arylamides is to be undertaken.

EXPERIMENTAL

The Chloroanilides. The chloroanilides were prepared as follows: the anilide was dissolved in either a mixture of carbon tetrachloride and acetic acid (10:1 by volume) (A), methanol (B), or in a mixture of methanol and glacial acetic acid (2:1 by volume) (C). An equimolecular quantity of tertiary butyl hypochlorite was added when the solution became warm. Where carbon tetrachloride was used as the solvent the reaction mixture was allowed to stand 2-3 hours while crystals of the chloro-anilide separated. Where methanol was used the reaction mixture was poured into water to precipitate the chloroanilide.

The following table summarises the results obtained with seven anilides:

Anilide	Solvent	Chloroanilide	m.p. (uncorr.)	Yield %
acetanilide	A	4-chloroacetanilide	176°	65
		2-chloroacetanilide	87°	trace
propionanilide	B	4-chloropropionanilide	138-140°	*
benzanilide	A	4-chlorobenzanilide	191-192°	60
		2-chlorobenzanilide	115-117°	trace
aceto-*p*-toluidide	B	3-chloro-4-acetamino-toluene	116°	60
aceto-*o*-toluidide	B	5-chloro-2-acetamino-toluene	144-145°	95
aceto-α-naphthalide	C	4-chloro-α-aceto-naphthalide	191-192°	77
aceto-β-naphthalide	C	1-chloro-β-aceto-naphthalide	149-151°	92

*Not determined. 1·0 g. propionanilide gave 0·9 g. of a mixture containing 4-chloropropionanilide.

The Chloramides. The amide was dissolved in a mixture of carbon tetrachloride and glacial acetic acid (4:1 by volume) and an equimolecular quantity of tertiary butyl hypochlorite added. After allowing the yellow colution to stand for 18 hours the solution became a pale straw colour when crystals of the N-chloroamide separated in good yield. In this way benzamide gave N-chlorobenzamide, m.p. 117-118° (70 *per cent.*). and acetamide gave N-chloroacetamide, m.p. 108-110° (60 *per cent.*). Both compounds liberated iodine from potassium iodide solution.

*N-Chloro-*p*-toluenesulphonamide.* *p*-Toluenesulphonamide was dissolved in methanol, an equimolecular quantity of tertiary butyl hypochlorite added, the reaction mixture poured into water and the white precipitate filtered off and dried over phosphorus pentoxide; m.p. 61-62° (70 *per cent.*). The product liberated iodine from potassium iodide.

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REACTIONS OF TERTIARY BUTYL HYPOCHLORITE. PART II. N-CHLORINATION OF ANILIDES

by **J. S. CHALSTY and S. S. ISRAELSTAM**

OPSOMMING

N-Chlooranilide word verkry deur behandeling van anilide met tersiêre butiel hipochloriet in die teenwoordigheid van boraks. Verskeie nuwe N-chlooranilide is volgens hierdie metode berei.

SUMMARY

N-Chloroanilides are obtained by the action of tertiary butyl hypochlorite on anilides in the presence of borax. A number of new N-chloroanilides have been prepared by this method.

Although Audrieth, Colton and Jones[1] claim to be the first to use tertiary butyl hypochlorite as an N-chlorinating agent, Clark[2] reported the formation of N-chloroamides by the action of tertiary butyl hypochlorite on amides many years earlier. In Part I[3] it was reported that N-chlorobenzamide and N-chloroacetamide could be readily obtained in a similar manner.

This paper describes a convenient method for obtaining N-chloroanilides in good yield by treating a methanolic solution of the anilide with tertiary butyl hypochlorite in the presence of borax which prevents rearrangement to the nuclear chloroanilide.

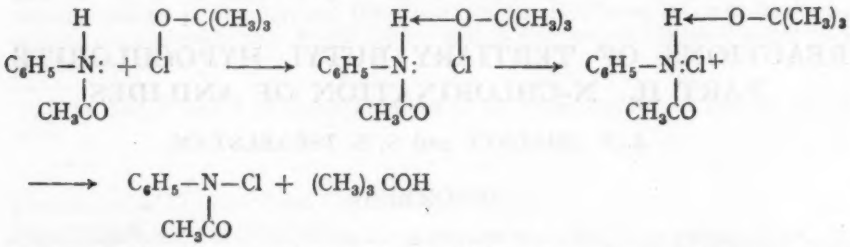
Bender[4] was the first to prepare N-chloroacetanilide by the action of an alkali hypochlorite on acetanilide. Alkaline conditions were also found necessary for N-chlorination by Chattaway and Orton[5] who used an alkali hypochlorite in the presence of potassium carbonate in aqueous media.

The methods reported in the literature for the N-chlorination of anilides are generally tedious and chlorinations are carried out in a heterogeneous system with subsequent low yields. The advantages claimed for the use of tertiary butyl hypochlorite are that it provides an excellent source of reactive chlorine atoms, at the same time eliminating any possibility of hydrolysis of the product due to a high alkaline concentration and the product is easily isolated from the reaction mixture.

A preliminary series of experiments was carried out using acetanilide in methanol and tertiary butyl hypochlorite to find a suitable base for N-chlorination. With pyridine and calcium oxide acetanilide gave 4-chloroacetanilide; with sodium hydroxide extensive decomposition occurred, and no product could be isolated. Zimmer and Audrieth[6] have reported the formation of N-chloroacetanilide in very poor yield by the interaction of tertiary butyl hypochlorite and acetanilide in the presence of 0·5 N sodium hydroxide. The chief product of that reaction, however, was 4-chloroacetanilide. With borax a 95 *per cent.* yield of pure N-chloroacetanilide resulted, the reaction being almost instantaneous. Since borax is appreciably soluble in methanol the reaction was carried out in a homogenous solution. Sodium acetate was also found to be satisfactory.

By using borax a large number of N-chloroanilides shown in Table I were obtained, among them nine new N-chloroanilides. An N-chloro-derivative was not obtained from salicylanilide; instead, 2-hydroxy-5-chlorobenzanilide obtained by Shilov and Bogdanov[8] by a different method, was isolated. This compound was probably formed by the rearrangement of N-chlorosalicylanilide.

The following mechanism based on that of Mauger and Soper[7] is suggested for the N-chlorination of anilides by tertiary butyl hypochlorite:



This mechanism assumes that there is a preliminary formation of a hydrogen bond between the amino hydrogen atom and the oxygen atom in the hypochlorite molecule acting as a donor atom, followed by electron release by the chlorine atom to form a chlorinium ion.

Mono-substituted N-chloroanilides rearranged without much difficulty, no particular substituent having any inhibitory effect. However, the presence of two or three substituents on the benzene ring rendered the rearrangement progressively more difficult. Thus, N-chloroacetanilide rearranged readily to 4-chloroacetanilide simply by shaking the former with glacial acetic acid and dilute hydrochloric acid; N,4-dichloroacetanilide rearranged more slowly and N,2,4-trichloroacetanilide required heating with hydrochloric acid.

N-Chloroanilides were analysed by determining the iodine liberated from potassium iodide by these compounds with standard sodium thiosulphate. The lower melting points of some N-chloroanilides reported by other authors were probably due to impurities since in a few cases those compounds with relatively low melting points were shown to have low chlorine contents. The N-chloroanilides were best kept in a desiccator after crystallisation.

EXPERIMENTAL
(M.p.'s are uncorrected)

N-Chloroanilides. In general the procedure adopted was as follows: the anilide (6-10 g.) was dissolved in a 4 *per cent.* solution of borax in methanol and slightly more than an equimolecular quantity of tertiary butyl hypochlorite was added slowly with shaking. In the case of phenacetin and aceto-*o*-toluidide the hypochlorite was added at −8°. No change of temperature occurred and the solution remained alkaline to litmus. On pouring into water or on to crushed ice, the N-chloroanilide separated in excellent yield; it was crystallised from light petroleum and dried over phosphoric oxide. Table I summarises the preparation of the various anilides.

In the following cases the treatment of the reaction mixture was modified: *N-chloro-α (and β)-naphthalides:* when the reaction mixture was poured into water the N-chloro-compound separated as a white colloidal suspension which on standing turned yellow and then blue-green. Rubbing with a glass rod caused the deposition of a white precipitate. *N-chloroaceto*-p-*phenetide* and *N-chloro-aceto*-o-*anisidide:* these two compounds were precipitated when their respective reaction mixtures were poured on to crushed ice. The precipitate in each case was filtered off as rapidly as possible, but could not be dried or recrystallised since it decomposed in air. A portion which was partially dried by washing with a little dry ether was found to melt at 30-34° and the chlorine analysis indicated a purity of 80 *per cent.* The N-chloroaceto-*o*-anisidide, m.p. 22-25° (decomp.) was found to be even more unstable

than the phenetide. Although the compound liberated iodine from potassium iodide no quantitative analysis could be carried out owing to the rapid decomposition of the compound.

Reaction between salicylanilide and tertiary butyl hypochlorite. Salicylanilide (6·4 g., 0·03 mole) was dissolved in a 4 *per cent.* methanolic solution of borax and tertiary butyl hypochlorite added (3·6 ml., 0·033 mole). The reaction mixture was poured into cold water or on to crushed ice, acidified with acetic acid and the precipitate (6·2 g.) immediately filtered off. The substance did not liberate iodine from potassium iodide and on crystallising from ethanol it had m.p. 206-208°. Although this reaction was carried out at various temperatures and without borax, the same compound was obtained. The melting point of this compound agreed with that reported by Shilov and Bogdanoc[8] for 2-hydroxy-5-chlorobenzanilide.

TABLE I

N-Chloroanilide	Yield %	M.P. (uncorr.)	% Cl as N-Cl Found	Calc.	M.P. (literature)
N-chloroacetanilide	96	91°	20·94	20·94	91°; Chattaway and Orton[9]
N,4-dichloroacetanilide ..	97	82°	17·38	17·40	82°; *loc. cit.*
N,2,4,-trichloroacetanilide	90	78°	14·75	14·86	78°; *loc. cit.*
N,2,4,6-tetrachloroacetanilide	88	74°	12·96	13·00	74°; Chattaway and Orton[10]
N-chloropropionanilide ..	99	77-78°	19·34	19·36	77°; Chattaway and Orton[11]
N-chlorobenzanilide	100	85°	15·42	15·35	77°; Chattaway and Orton[9] 81·5-82°; Slosson[12]
N-chloroaceto-α-naphthalide	90	92-93°	16·19	16·16	75°; *loc. cit.* 80°; Hoogeveen[13], a
N-chloroaceto-β-naphthalide	86	90-91°b	16·10	16·16	80°; Hoogeveen[14]
N-chloro-aceto-o-toluidide	100	43°	19·40	19·36	43°; Chattaway andOrton[15]
N-chloro-aceto-p-toluidide	99	91-92°	19·33	19·36	91°; *loc. cit.*
N-chloropropio-o-toluidide	95	47-48°	17·95	17·97	Not reported
N-chloropropio-p-toluidide	99	71-72°	18·03	17·97	,, ,,
N-chlorobenzoyl-o-toluidide	93	78°	14·46	14·41	,, ,,
N-chlorobenzoyl-p-toluidide	98	110-111°	14·41	14·41	,, ,,
N-chlorobenzoyl-α-naphthalide	92	106°	12·60	12·61	,, ,,
N-chlorobenzoyl-β-naphthalide	90	95-96°	12·59	12·61	,, ,,
N-chloro-o-bromoacetanilide	99	86°	14·26	14·26	86°; Chattaway and Wadmore[16]
N-chloro-m-bromoacetanilide	75	69°	14·23	14·23	Not reported, c.
N-chloro-p-bromoacetanilide	97	109°	14·22	14·26	108-109°; Chattaway and Orton[18]
N-2-dichloro-4-bromoacetanilide	80	89°	12·48	12·54	88-89°; *loc. cit.*
N,2,6-trichloro-4-bromoacetanilide	83	80-81°	11·13	11·18	81°; *loc. cit.*
N-chloro-o-bromopropionanilide	92	59°	13·54	13·52	59°; Chattaway[19]
N-chloro-p-bromopropionanilide	90	59°	13·47	13·52	59°; *loc. cit.*
N-chloro-o-bromopropionanilide	99	85°;	11·38	11·40	85°; Chattaway and Wadmore[16]
N-chloroformanilide	99	47°	22·80	22·83	47°; Chattaway and Orton[9]
N-chloroformyl-p-toluidide	99	58-59°	20·80	20·81	49-50°; Slosson[12], d
N-chloro-o-nitroacetanilide	92	80-81°	16·54	16·47	80°; Chattaway, Evans and Orton[20]
N-chloro-p-nitroacetanilide	88	114°	16·45	16·47	110-111°; *loc. cit.*
N-chloro-aceto-p-phenetide	e	30-34°	e		Not reported
N-chloroaceto-o-anisidide	e	22-25°	e		,, ,,

a. This author reported 97 *per cent.* purity; b. After standing for 8 days the percentage purity decreased to 92 and the m.p. to 79-81·5°; c. Mentioned by Fontein[17] but not isolated by him; d. This low m.p. must be due to impurity; e. The yield could not be determined and the percentage chlorine as N-Cl could not be determined due to decomposition.

Rearrangements. The rearrangement of the N-chloroanilide was carried out by dissolving it in glacial acetic acid and shaking with dilute hydrochloric acid. In most cases the solution became warm and turned slightly yellow. In a few cases the solution required heating. After pouring into water the nuclear chloroanilide separated. Table II summarises the various rearrangements.

TABLE II

N-Chloroanilide	Experimental condition	Nuclear chloroanilide
N-chloroacetanilide	Shaking with dil. HCl	4-chloroacetanilide
N,4-dichloroacetanilide ..	Shaking with dil. HCl for 5 min.	2,4-dichloroacetanilide
N,2,4-trichloroacetanilide ..	Heating with conc. HCl ..	2,4,6-trichloroacetanilide
N-chloro-p-bromoacetanilide	Shaking with dil. HCl	2-chloro-4-bromoacetanilide
N,2-dichloro-4-bromoacetanilide	Heating with conc. HCl ..	2,6-dichloro-4-bromoacetanilide

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REACTIONS OF TERTIARY BUTYL HYPOCHLORITE. PART III. THE PREPARATION OF HYDRAZINE FROM UREA

by **J. S. CHALSTY and S. S. ISRAELSTAM**

OPSOMMING

Monochloorureum (N-chloorureum) en hidrasien is berei deur behandeling van ureum met tersiêre butiel hipochloriet.

SUMMARY

Monochlorourea (N-chlorourea) and hydrazine have been prepared by the action of tertiary butyl hypochlorite on urea.

The manufacture of hydrazine on an industrial scale has aroused much interest and attempts have been made to improve its method of manufacture. Further, since hydrazine is formed from sodium hypochlorite and urea (Schestakoff[1], Das and Mukherji[2] and others[3, 4, 5, 6]), it was decided to investigate its preparation from urea and tertiary butyl hypochlorite. Whilst this work was in progress Audrieth, Colton and Jones[7] reported that when tertiary butyl hypochlorite was refluxed with a large excess of urea in the presence of sodium hydroxide and gelatin, a yield of 36 *per cent.* of hydrazine as the crude salicylazine, was obtained.

For the formation of hydrazine from urea and sodium hypochlorite, Schestakoff[1] proposed a mechanism based upon the Hofmann degradation of acid amides to primary amines, according to which monochlorourea is an intermediate in this reaction. Although Audrieth, Colton and Jones'[7] attempt to isolate it was unsuccessful, they reported that the spectra of solutions containing both urea and tertiary butyl hypochlorite indicated the formation of a compound containing an N-Cl linkage.

We have re-investigated the preparation of monochlorourea from urea and tertiary butyl hypochlorite. When equimolecular quantities of tertiary butyl hypochlorite and urea dissolved in methanol were mixed at 0°, careful evaporation of the solvent gave an excellent yield of monochlorourea. Behal and Detoeuf[8] reported the formation of this compound by the action of gaseous chlorine on an aqueous solution of urea at 15°.

The conversion of monochlorourea to hydrazine should, according to the mechanism proposed by Schestakoff, be brought about by sodium hydroxide. When an aqueous solution of monochlorourea was boiled with an excess of sodium hydroxide in the presence of gelatin and the solution allowed to cool, hydrazine was formed and isolated in excellent yield either as the sulphate or as benzalazine. Hydrazine was also obtained in excellent yield by the addition of a chilled methanol solution containing tertiary butyl hypochlorite and urea to an aqueous solution of sodium hydroxide and gelatin and boiling. The method of Audrieth, Colton and Jones

involving the addition of tertiary butyl hypochlorite to a mixture of sodium hydroxide and urea, resulted in extensive decomposition and low yields of hydrazine.

EXPERIMENTAL

Monochlorourea. Urea (15 g., 0·25 mole) was dissolved in methanol and chilled to 0°. Tertiary butyl hypochlorite (30 ml.) was added slowly with constant shaking. The temperature rose to 5° and the solution became pale yellow. About 3-4 ml. of this solution were poured into each of a number of small watch glasses and the methanol allowed to evaporate slowly. Solid white residues of monochlorourea, m.p. 79-80° (22·8 g., 97 *per cent.*) were thus obtained; no visible decomposition took place (Found: Cl as NCl, 37·0%; CH_3ON_2Cl requires: Cl, 37·6%). Behal and Detoeuf[8] give m.p. 71°.

Hydrazine. (a) From monochlorourea: sodium hydroxide (6 g.) and 5% gelatine (20 ml.) in 200 ml. water were cooled to 0°. Monochlorourea (6 g.) was added slowly with constant shaking. When all the monochlorourea had dissolved, the solution was warmed gently and then boiled under reflux for 40 minutes, cooled and divided into two equal portions. The first portion was treated with sulphuric acid and cooled to 0° when hydrazine sulphate separated, m.p. 256° (3·4 g., 85 *per cent.*). The second half of the solution was treated with a slight excess of benzaldehyde, shaken thoroughly and the emulsion just dissolved by the addition of ethanol. On cooling to 0° benzalazine separated (6·0 g., 92 *per cent.*) and was recrystallised from dilute ethanol in long yellow needles, m.p. 94°.

(b) From urea, tertiary butyl hypochlorite and sodium hydroxide: urea (5 g.) was dissolved in methanol, the solution cooled to 0° and tertiary butyl hypochlorite (10 ml.) added slowly. This solution was poured slowly into a solution of sodium hydroxide (8 g.) and 5 *per cent.* gelatin (30 ml.) in 300 ml. water, also at 0°. The solution was gradually heated and then boiled under reflux for 40 minutes. On cooling and treating with benzaldehyde, benzalazine was obtained, m.p. 94° (14·4 g., 94 *per cent.*).

The authors wish to thank Professor O. G. Backeberg for his interest in the work, and one of us (J.S.C.) thanks the S.A.C.S.I.R. for a bursary.

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THE ACCURATE DETERMINATION OF CALCIUM AND MAGNESIUM IN PLANT MATERIALS

by **W. J. A. STEYN**

OPSOMMING

Die belangrikste faktore wat die vlamfotometriese en volumetriese bepaling van kalsium en magnesium beinvloed, is ondersoek. Daar word gewys dat sodra fosfaat en sulfaat ione verwyder word uit die toetsoplossing, die nadelige invloed van ander elemente of geheel en al verdwyn, of baie verminder word. Snel metodes vir die noukeurige bepaling van kalsium, natrium, kalium (vlamfotometries) en kalsium en magnesium (volumetries), nadat nadelige ione verwyder is deur middel van ion-uitruiling, word beskrywe.

SUMMARY

A critical investigation of the interferences likely to occur in the flame-photometric and volumetric determination of calcium and magnesium is presented. It is shown that all interferences may either be eliminated or much suppressed by the removal of phosphate and sulphate ions from the test solution. Rapid methods are described for the accurate determination of calcium, sodium, potassium (flame-photometric) and calcium and magnesium (volumetric) after removal of interfering ions by ion-exchange.

Various workers[1, 2, 3, 4] have reported the interference of several ions, particularly of phosphates, in the versenate(EDTA) titration of calcium and magnesium. The interference of phosphate, sulphate and other ions has been reported in the flame-photometric determination of calcium[5, 6, 7, 8]. More or less satisfactory methods for the flame-photometric determination of calcium in air:acetylene mixtures have been worked out[5, 6, 8]. These methods, however, do not hold for the "cold" flame of the air : propane mixture used, for example, in the "Eel" flame-photometer. The removal of interfering phosphates has been satisfactorily accomplished by the use of anion-exchange resins for the EDTA determination of calcium[9, 10, 11].

The work described here was undertaken in order to investigate existing methods with a view to modifying them for rapid and accurate routine analysis of soils and plant materials.

EXPERIMENTAL

Apparatus and reagents. The flame-photometric work was carried out on the "Eel" of Evans Electroselenium, Limited. "Bottogas" was used with compressed air; the variation in the pressure of the town gas supply was such that accurate results could not be obtained with it. The low-heat flame of the "Eel" is admirable for the accurate determination of calcium, sodium and potassium since interference from emission by foreign elements is less likely than with hotter flames. All standard solutions and solutions containing interfering ions were prepared from Johnson Matthey "Specpure" chemicals. All other reagents were of "Analar" grade.

Interfering ions in the EDTA titration of Calcium and Magnesium. Controlled experiments were carried out on standard solutions containing varying amounts of the foreign ions likely to interfere in solutions of plant materials. The results are summarised below:

(i) *EDTA titration of Ca with screened murexide:* The indicator, murexide, was screened with naphthol green B to obtain a better end point in calcium titrations against EDTA. The end point was a clear dark blue without a trace of violet, was very definite, stable and much easier to recognise than when murexide alone was used.

Magnesium had no influence on the recovery of calcium between Ca/Mg ratios of 10:1 and 1:10. The only effect of phosphate between ratios of Ca/P from 15:1 to 1:4 was to delay the end point when the ratios became smaller than 3:1. Quantitative results for Ca were still obtained up to a ratio of 1:4 even though solid calcium phosphate was formed, provided the titration was continued with shaking to the stable end point.

When phosphate and heavy metals were present, however, the end point deteriorated rapidly with increasing concentration of heavy metals. The concentration of some heavy metals which could simultaneously be present with phosphate without interfering with the quantitative recovery of calcium were found to be:

Fe^{3+}, 10 *per cent.*; Mn^{2+}, 1 *per cent.*; Cu, ½ *per cent.* and Zn, ½ *per cent.* of the Ca. concentration.

The phosphorus in the solution was double the concentration of the Ca. When phosphorus was absent from the test solution, the amounts of heavy metals could be doubled without showing interference, a fact which seems to have been overlooked by previous workers.

(ii) *EDTA titration of Ca+Mg with Eriochrome Black T:* Standard solutions containing varying amounts of Ca, Mg, Na, K, Fe^{3+}, Mn^{2+}, Cu, Zn, and B were titrated against EDTA with Eriochrome Black T as indicator, both in the presence as well as in the absence of phosphate. Ferric iron interfered with the colour change of the indicator, apparently oxidising the indicator with the result that no change in colour was observed. Increased amounts of Mn^{2+} enhanced the interference of iron. In the presence of phosphorus, Fe^{3+} began to interfere when present in amounts greater than 1·5 *per cent.* of the Ca+Mg content. However, in the absence of phosphorus, Fe^{3+} could be present in amounts up to 25 *per cent.* of the Ca+Mg content without interfering.

A synthetic standard solution containing a mixture of different elements in the proportions listed below, was titrated against EDTA with Eriochrome Black T as indicator. The recovery of Mg was quantitative and no deterioration of the end point was observed (phosphate absent):

Ca	Mg	Na	K	Fe^{3}	Mn^{2}	Cu	Zn	B
20	1	1	40	5	0·1	0·02	0·02	0·02

Thus in the absence of phosphate the EDTA method for determining magnesium with Eriochrome Black T as indicator is very suitable for plant materials in which the concentrations of trace elements seldom exceed the figures given above. The titration was sensitive and accurate in the absence of phosphorus.

Interfering ions in the flame-photometric determination of Ca. The interference of phosphate, sulphate and some other ions in the flame-photometric determination of calcium has been reported by several workers[5, 6, 7, 8]. Some of these interferences were investigated using an "Eel" flame-photometer with an air : 'bottogas'" mixture.

Standard solutions containing varying concentrations of calcium, phosphate, sulphate and foreign cations were tested for the recovery of Ca. The suppression by sulphate and phosphate ions of the emission by calcium is shown diagramatically in Fig. 1, and is so serious that calcium cannot be determined accurately on the "Eel" unless these anions are removed from the test solution.

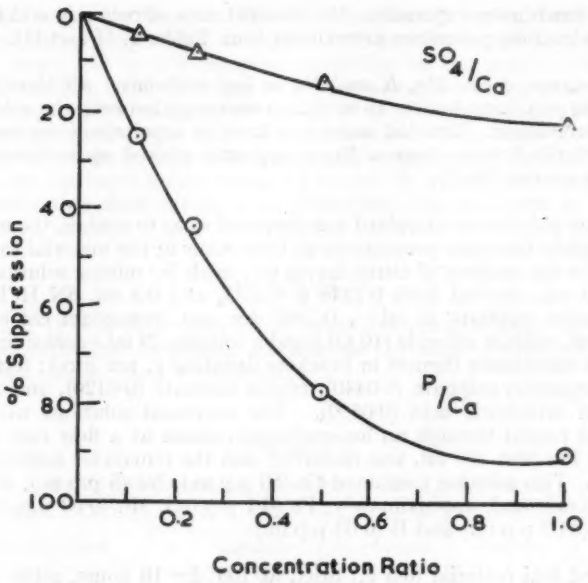

Fig. 1
Suppression of Ca by PO_4 and SO_4.

Magnesium had no effect on the emission of Ca for Ca/Mg ratios from 10:1 to 1:3. When the ratio was 1:4 and smaller, Mg suppressed the emission of Ca, the error being about 6 *per cent.* for a ratio of 1:8. This ratio, however, never occurs in plant materials and only very seldom in soils.

A synthetic standard solution containing a mixture of different cation chlorides in the proportions listed below, showed no interference with the recovery of Ca on the "Eel":

Ca	Mg	Na	K	Al	Fe^3	Mn^2	Cu	Zn	B
20	10	10	40	2	0·5	0·2	0·1	0·1	0·1

It is clear, therefore, that if phosphate and sulphate are absent, other elements normally occurring in plant materials will not interfere in the determination of calcium on a low-heat flame-photometer. It is of interest that the relatively high concentration of potassium showed no interference with calcium on the "Eel", whereas Strasheim and Nell[6] reported a suppression by K of the Ca emission when using an air:acetylene mixture. The author actually obtained quantitative recovery of Ca on the "Eel" from chloride solutions in which the K/Ca ratio was as much as 6:1.

Removal of phosphate and sulphate by ion-exchange. Exhaustive experiments were carried out with various anion exchange resins to find a suitable and rapid means for the quantitative removal of polyvalent anions from the test solution prior to the determination of calcium and magnesium. This was satisfactorily accomplished with the resin, De-Acidite E, obtained from Hopkin and Williams, England. Similar results were obtained with the American equivalent, Amberlite IR-4B, which

is, however, much more expensive. The completeness of recovery and the reproducibility of the leaching procedure are evident from Tables I, II and III.

Determination of Ca, Mg, K and Na in leaf materials. All standard solutions were stored in polythene bottles to avoid ion-exchange between the solution and the walls of the container. Distilled water was kept in a polythene aspirator as it was found that distilled water from a Pyrex aspirator picked up sufficient calcium to be detectable on the "Eel".

The flame-photometer standard was prepared so as to contain the main elements in approximately the same proportions as they occur in the material to be analysed. A standard for the analysis of citrus leaves was made by mixing solutions of calcium chloride (100 ml., derived from 0·1248 g. $CaCO_3$ and 0·3 ml. 5N HCl), 0·2535 *per cent.* magnesium sulphate (3 ml.) , 0·1907 *per cent.* potassium chloride (10 ml.), 0·1271 *per cent.* sodium chloride (10 ml.) and a solution (3 ml.) containing the following hydrated substances (figures in brackets denoting g. per litre): ferrous sulphate (0·1659), manganous sulphate (0·0440), cupric sulphate (0·0120), and zinc sulphate (0·0500), and orthoboric acid (0·0500). The combined solutions were diluted to 1000 ml. and passed through an ion-exchange column at a flow rate of two drops per second. The first 100 ml. was discarded and the remainder collected in a polythene bottle. This solution contained Ca (50 p.p.m.), Na (5 p.p.m.), K (10 p.p.m.), Mg (0·75 p.p.m.), and, approximately, Fe (0·1 p.p.m.), Mn (0·03 p.p.m.), Cu (0·009 p.p.m.), Zn (0·03 p.p.m.) and B (0·03 p.p.m.).

Powdered leaf material (0·5 g.) dried at 105° for 16 hours, nitric acid (10 ml.) and about 65 *per cent.* perchloric acid (2 ml.) were digested in a 150 ml. conical flask fitted with a cover glass at a very low heat until the vigorous reaction subsided and then boiled until most of the solid particles had dissolved (usually about 1 hour). With the cover glass removed the solution was evaporated to dryness; any colouration in the residue was removed by adding a few drops of perchloric acid and evaporating again to dryness. The colourless residue was dissolved in water acidified with a few drops of 5N HCl, filtered and diluted to 100 ml.

The solution (10 ml.) thus prepared was adjusted to pH 3-4 by adding 10 *per cent.* ammonium carbonate (the required amount of which had previously been determined with the aid of methyl orange) and passed through a column (2 cms. diameter) of De-Acidite E resin in the chloride form (about 15 g., previously washed with 5 *per cent.* sodium carbonate, distilled water, 5 *per cent.* hydrochloric acid and finally distilled water until the washings were free of colour) at a rate of 1 drop per sec. The resin was washed with distilled water at the same flow rate until a total volume of 100 ml. had been collected.

Ca, Na and K were determined in the leachate without further dilution on the "Eel" flame-photometer. The instrument was calibrated by spraying the standard and adjusting the potentiometer control to give full-scale deflection on the lower linear scale for Ca (50 p.p.m.), Na (5 p.p.m.) and K (10 p.p.m.) respectively. The zero was set by spraying distilled water.

Ca+Mg was determined by titrating 50 ml. of the leachate, diluted to 100 ml. and containing 5 ml. of ammonium chloride buffer (67·4 g. and 570 ml. concentrated ammonia per litre) and 15 small drops of 0·4 *per cent.* Eriochrome Black T (in methanol containing 4 *per cent.* hydroxylamine hydrochloride) against 0·01 normal EDTA to a stable clear blue endpoint. Magnesium was obtained by subtracting the value due to the Ca (determined flame-photometrically) from the titer.

Perchlorate ions were found to be mainly responsible for exhausting the resin, hence the necessity of evaporating as much of the perchloric acid as possible during the digestion stage. 10 to 100 Samples, depending on the perchlorate content in plant residue, could be leached through the same column before regeneration of the resin was necessary. The resin was exhausted when phosphate could be detected in the leachate (molybdenum blue test). For routine analysis, a battery of 12 columns was prepared, the whole operation of leaching 12 samples and determining Ca, Na, K and Mg in the leachates taking about 1½ hours. It was better to regenerate the resin in an erlenmeyr flask rather than performing the operation in the column itself.

RESULTS

In Tables I, II and III experimental results showing the reproducibility and accuracy of the method are tabulated. In each case the solutions were passed through the ion-exchange column prior to analysis.

TABLE I

RECOVERY TESTS FROM SYNTHETIC STANDARDS

Foreign ions added			Calcium		Magnesium		Sodium		Potassium	
P p.p.m.	SO_4 p.p.m.	Fe:Mn:Cu:B:Zn p.p.m.	Theor. p.p.m.	Found p.p.m.	Theor. p.p.m.	Found p.p.m.	Theor. p.p.m.	Found p.p.m.	Theor. p.p.m.	Found p.p.m.
10	10	1:·05:·05:·05:·05	40	40·0	2	1·98	2	2·0	6	5·9
20	10	,,	40	39·5	2	2·01	2	2·1	6	6·0
50	10	,,	40	40·0	2	1·99	2	2·0	6	6·1
100	10	,,	40	40·0	2	2·02	2	1·9	6	5·8
200	10	,,	40	39·0	2	1·97	2	2·0	6	6·0

TABLE II

RECOVERY TESTS FROM PLANT SOLUTIONS

Calcium		Magnesium		Sodium		Potassium	
Added p.p.m.	Found p.p.m.	Added p.p.m.	Found p.p.m.	Added p.p.m.	Found p.p.m.	Added p.p.m.	Found p.p.m.
25	24	4·19	4·18	1·35	1·30	3·5	3·4
30	29	2·84	2·85	1·85	1·75	4·5	4·3
35	34	3·58	3·60	2·35	2·30	5·5	5·3
40	39	4·32	4·34	2·85	2·80	6·5	6·5
45	43	5·07	5·10	3·35	3·30	7·5	7·3
50	49	5·81	5·83	3·85	3·85	8·5	8·5

TABLE III

REPRODUCIBILITY OF LEACHING AND DIGESTION PROCEDURE
(Citrus Leaves)

No.	Wt. Leaves g.	Calcium %	Magnesium %	Sodium %	Potassium %
1	0·5238	3·74	0·46	0·16	0·35
2	0·4976	3·77	0·50	0·17	0·35
3	0·5012	3·76	0·48	0·16	0·34
4	0·5024	3·72	0·45	0·16	0·35
5	0·4864	3·77	0·50	0·15	0·34
6	0·5312	3·75	0·47	0·17	0·36
6	0·5167	3·77	0·50	0·17	0·35
8	0·5087	3·73	0·45	0·16	0·35
9	0·4952	3·75	0·47	0·16	0·34
10	0·5126	3·77	0·50	0·15	0·35
11	0·4856	3·76	0·49	0·16	0·33
12	0·5267	3·76	0·50	0·17	0·35
MEAN		3·75	0·48	0·16	0·35
Standard Deviation ..		0·018	0·02	0·008	0·01
% Standard Deviation ..		0·5	4·2	5	2·9

DISCUSSION

The digestion procedure was specially developed to provide a rapid means of dissolving plant material. The cover glass on the digestion flask (a funnel-shaped cone with a short tapered glass rod fused on the apex and extending to about ½ inch above the liquid in the flask) acted as a condenser which economised on the consumption of nitric acid. Twelve to twenty-four leaf samples could comfortably be brought into solution within 4 hours, depending on the size of hotplate available. The digestion proceeded smoothly and needed a minimum of attention.

From the tables it is clear that leaching was quantitative—all the phosphate and sulphate ions were removed from the test solution, while Ca, Mg, Na and K ions were not retained by the resin. All the anions in the test solution were exchanged for chloride ions. The leaching procedure was rapid when carried out on a routine basis.

There is no doubt that the removal of all anions except chloride from the test solution rendered both the versenate and the flame-photometric method accurate and reproducible. The reproducibility, as indicated in Table III, was well within the experimental error to be expected from normal chemical methods.

Since the development of the method, it has been used successfully and extensively by two assistants for the routine determination of Ca, Mg, Na and K in the leaves of various crops, particularly of citrus and of pineapples. It has also been successfully applied to the determination of exchangeable cations in soils.

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A SIMPLIFIED PROCEDURE FOR THE RAPID DETERMINATION OF APPARENT DIPOLE MOMENTS IN SOLUTION

by **J. A. van den BERG**

OPSOMMING

'n Vereenvoudigde metode word beskryf vir die bepaling van dipoolmomente in oplossing met behulp van 'n nuwe tipe sel en 'n gewysigde heterodien-kapasiteitsmeter.

SUMMARY

A simplified method is described for the determination of dipole moments in solution by means of a new type of cell and modified heterodyne capacity meter.

Although the classical Debye equation is not strictly valid for solutions and should be replaced by a more accurate equation such as that of Bottcher[1] for pure liquids, the use of solutions is preferable for determining dipole moments when only small quantities of the polar substances are available, when the liquid shows strong association or when the polar substance is a solid at room temperature. For stereochemical applications absolute values are unnecessary and solution data suffice[2] if the values are trustworthy.

In the usual method the densities and the dielectric constants of several solutions must be extrapolated to zero concentration. A single dipole moment determination is necessarily therefore a slow process. This procedure has been greatly accelerated by constructing a cell which was used for measurement of both density and dielectric constant. Transfering a volatile solution during the determination of the dipole moment was thereby completely eliminated. The cell was constructed in such a way that the polar substance could be added progressively and mixed efficiently without loss by volatilization.

EXPERIMENTAL

The cell, about 7 ins. high and capacity 100 ml., is depicted in Figure 1. The rotary 100 micromicrofarad condenser (A) could be fixed by means of arm (H) in the "open" or "closed" position. The spiral blade of the stirrer (B) ensured effective mixing. A tight-fitting polythene plate (G) provided electrical insulation and was covered on the inside with a coat (Q) of waterglass for protection against the organic solvent, benzene. The axles of the rotary condenser and of the stirrer (B) moved in a housing (P) of compressed felt which prevented the escape of vapour from the vessel. The mercury-containing sinker (C) was suspended from the beam of an analytical balance by means of a thin wire (D), diameter 0·01-0·02 mm. The pinhole (E), about 1 square mm., enabled the supporting wire to move freely. The solvent or polar substance was added through the ground-in stopper (F). The heights of the liquid in the vertical parts of the cell were equalised by means of the ground-in stopper (M). The screws (L and N) were connections for the capacity-meter.

The solutions were prepared by adding 5-10 drops of the polar substance at a time, and completely covered the condenser blades. The dielectric constant k was calculated from:

$$k=c_x/c$$

where c_x was the difference between the readings on the precision condenser (C_1 in fig. 2) when the rotary condenser of the cell was in its "closed" and "open" positions, while filled with the solution. When filled with air the difference was c scale divisions. An accuracy of 0·001 was obtained. The use of a parallel-plate condenser was no disadvantage [3].

The density d was given by:

$$d=d_oW/W_o$$

d being the density of water (25°), W and W_0 the weights of the sinker in the liquid and in water respectively. The accuracy was approximately 0·0001 g. per ml. Schulz [4] claimed a precision of 0·00001 if the weight of the sinker was nearly equal to its volume in ml.

The loss of vapour through the pinhole was negligible but was automatically taken into account when weight compositions were calculated from densities.

The capacity c_x or c was measured by means of the heterodynebeat method [5, 6]. In the circuit employed (fig. 2) the oscillator-stage described by Sahney *et al.* [7] and the mixer- and amplifier-stages described by Hudson *et al.* [8] have been modified and combined. Tubes T_1 and T_2 (both 6 SJ 7) were well isolated radio frequency oscillators. The frequency of T_1 was fixed at about 680 kilocycles per second while that of T_2 was put equal to that of T_1 by means of a calibrated variable condenser (C_1) (General Radio Co. precision condenser 722 D). The outputs from T_1 and T_2 were mixed in tube T_3 (6 L 7). The heterodyne signal was amplified by tube T_4 (6 C 5) to operate headphones and a cathode ray tube (X in fig. 2) so that the frequency matchpoint could be recognised both audibly and visually. The dielectric cell, which formed the testing condenser (C_2), was in parallel with the precision condenser (C_1). In the latter condenser the decrease in capacity required for the matching of the frequencies of T_1 and T_2, was equal to the capacity of the testing condenser (C_2). The use of the regulating tube (T_5) (VR 90) resulted in a stabilisation of the frequencies. The readings on the calibrated variable condenser were perfectly reproducible after a warming-up period of 30 minutes.

DISCUSSION

The suffix 1 refers to the solvent, 2 to the solute and 12 to the solution. The weight fraction w_2 of the solute is calculated from:

$$v_{12}=w_2v_2+(1-w_2)v_1$$

where v represents specific volume in ml. per g. This equation applies to dilute solutions, which were used in this method.

A convenient equation for the calculation is:

$$w_2=(v_{12}-v_1)/(v_2-v_1)$$
$$=(1/d_{12}-1/d_1)/(1/d_2-1/d_1)$$

where d represents density in g. per ml.

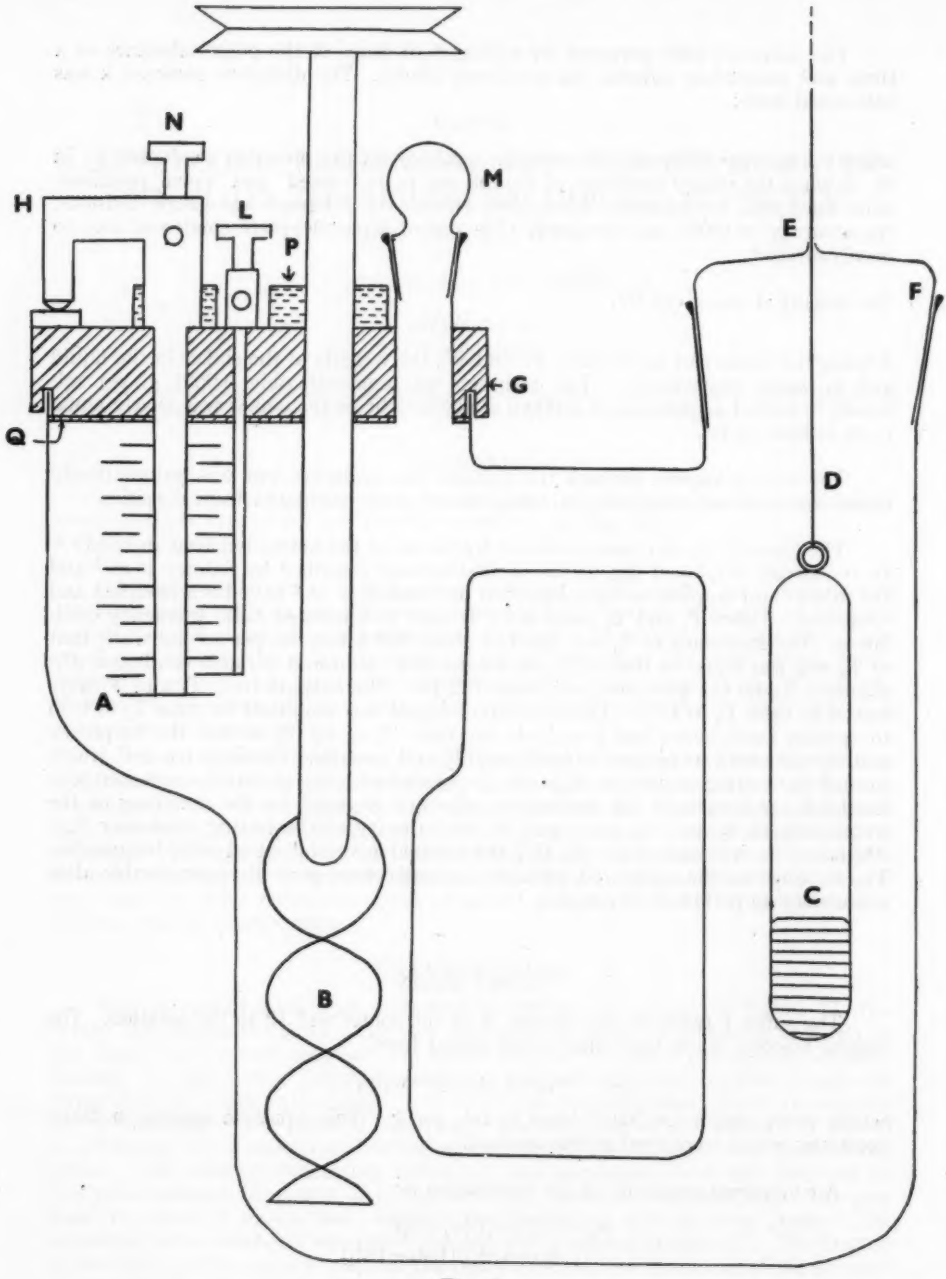

Fig. 1

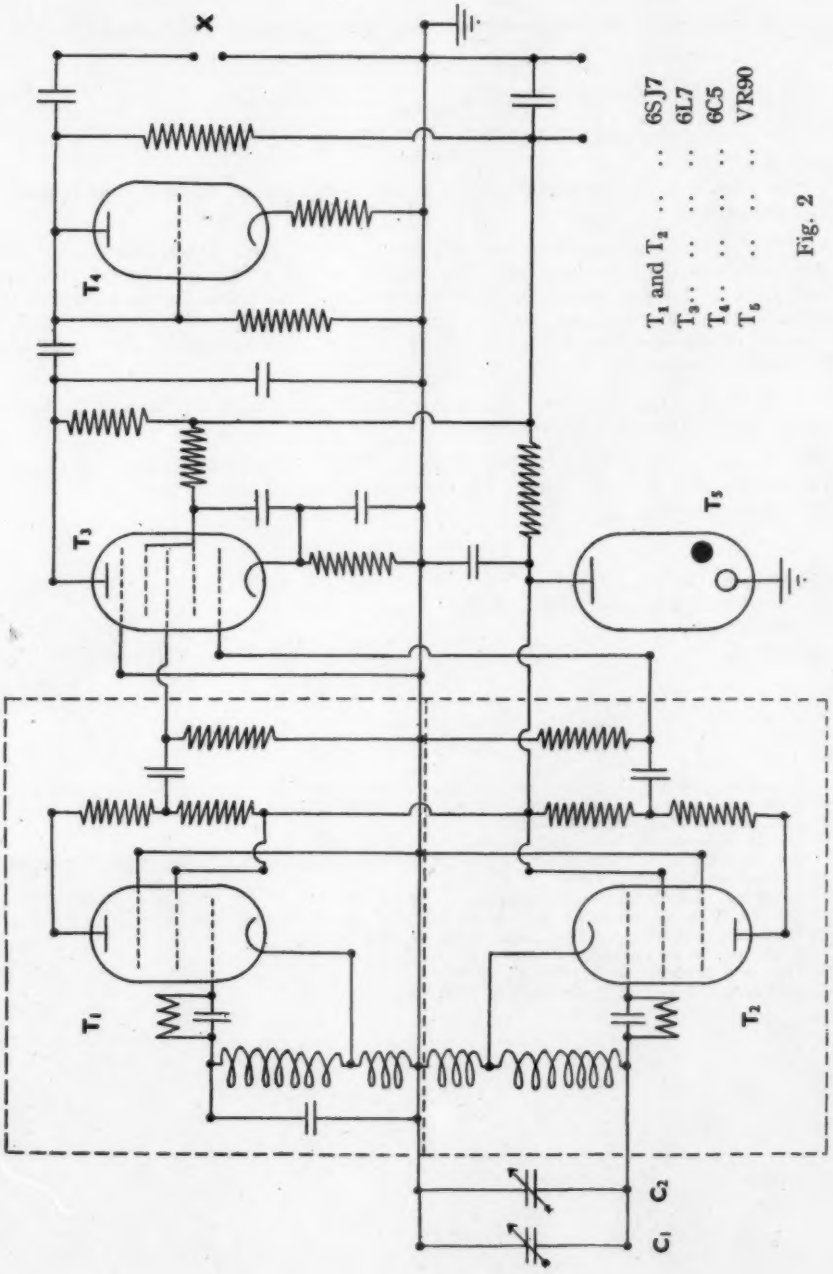

Fig. 2

At infinite dilution the specific polarisation p is given by Hedestrand's formula[6]:

$$_{0}p_{2}=3av_{1}/(k_{1}+2)^{2}-(v_{1}+b)(k_{1}-1)/(k_{2}+2)$$

$$\text{where } a=(\delta k_{12}/\delta w_{2})_{w_{2}=0}=\Sigma(k_{12}-k_{1})/\Sigma w_{2}$$

$$\text{and } b=(\delta v_{12}/\delta w_{2})_{w_{2}=0}=\Sigma(v_{12}-v_{1})/\Sigma w_{2}$$

a may also be found graphically from a plot of k_{12} against w_2 or b from a plot of v_{12} against w_2.

The method was tested for nitrobenzene and chloroform with benzene as solvent. The deviation from the mean for the dielectric constant k was 0·04 *per cent.* and 0·03 *per cent.* for the density d. The deviation from the mean for the values of the molar polarisation was one *per cent.*, giving values of 3·96±0·01 D for the dipole moment of nitrobenzene and 1·22±0·01 D for that of chloroform, in agreement with literature values[9,10,11].

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THE DETERMINATION OF SMALL QUANTITIES OF ACETALDEHYDE IN AQUEOUS SOLUTIONS

by N. R. M. IMPEY and E. T. VERDIER

OPSOMMING

Verskillende metodes vir die bepaling van klein hoeveelhede van asetaldehied is bestudeer en 'n geskikte volumetriese metode word beskryf.

SUMMARY

Different methods for the determination of small quantities of acetaldehyde in solution have been investigated and a suitable volumetric procedure has been developed.

In the course of an investigation of the anodic oxidation of calcium lactate solutions[1] it was found necessary to determine small quantities of acetaldehyde of the order of 0·2 g. to 0·5 g. per litre. In a review of the methods for the determination of aldehydes Reynolds and Irwin[2] have shown that most of the chemical methods mentioned in the literature are not suitable for the determination of small quantities of aldehydes in solution. Thus while Koltoff and Stenger[3] calculate that the theoretical inherent error (due to the dissociation of the aldehyde-bisulphite compound) in the determination of acetaldehyde by the bisulphite method should be of the order of 0·5 *per cent.* for 0·001 M solutions, Reynolds and Irwin state that for solutions 0·02 to 0·03 M the accuracy of the method is only 90 *per cent.* A critical investigation of the polarographic and certain volumetric methods was therefore undertaken.

Polarographic determination. In alkaline or neutral solutions acetaldehyde is reduced at the dropping mercury electrode giving a well defined wave at −1·9 v. (S.C.E.)[4, 5, 6, 7]. Quantitative results given in the literature are somewhat conflicting. Thus while Shikata *et al.*[4] and Smoler[5] have used this method for the determination of minute traces of acetaldehyde in alcoholic beverages and Elving and Rutner[6] obtained satisfactory results with solutions containing about 0·1 g. per litre, Dirscherl and Bergmeyer[8] found that special precautions had to be taken in order to obtain quantitative results.

Numerous determinations were therefore made under conditions similar to those reported by the above workers. Solutions containing 0·2 g. to 0·5 g. acetaldehyde per litre were made up with an indifferent electrolyte, 0·1 M with respect to lithium hydroxide and 0·01 M with respect to lithium chloride, and electrolysed between 1·3 and 2 volts. Oxygen was not removed as it does not interfere at these concentrations[5, 6]. The results were unsatisfactory owing to the rapid decrease with time of the acetaldehyde wave. To obtain the true wave height and results which might be reproducible, it would be necessary to obtain a series of curves at different times and extrapolate back to zero time. Because of the tediousness of such a determination, this method was abandoned in favour of a simpler volumetric procedure.

Volumetric determination. Of the various volumetric methods for the determination of acetaldehyde those depending on the formation of an aldehyde-bisulphite

compound appeared to be the best for estimating small quantities of the aldehyde. Of these, the method which consists of treating a measured volume of neutral aldehyde solution with an excess of neutralised sodium sulphite (thymolphthalein) and titrating the resulting mixture with standard acid to complete decolouration of the indicator[9, 3] cannot be used for small concentrations of aldehydes[2]. This leaves only iodimetric methods.

Originally Ripper[10] titrated directly the excess bisulphite with standard iodine, but this method has serious disadvantages[11]. Parkinson and Wagner[11], to overcome an inherent source of inaccuracy in the Ripper method, added an excess of iodine and back titrated with sodium thiosulphate solution. In this way the colour change at the end point, using starch indicator, was from blue to colourless which was preferable to the reverse[12].

The method of these two workers was thoroughly investigated to determine its suitability for the determination of acetaldehyde in dilute solutions, but the results were inconsistent.

Sodium bisulphite should be present in large excess to enable the equilibrium to be displaced in the direction favourable to formation of the aldehyde-bisulphite compound[3]. Under these conditions the bisulphite-iodine titration does not yield accurate results[12]; furthermore, some sulphur dioxide may be lost by volatilisation and some sulphite oxidised. A procedure which did not depend on the estimation of the excess bisulphite was therefore necessary. This was the case with the method used by Donnally[13] for the determination of formaldehyde and benzaldehyde, by Friedemann *et al.*[14] for the determination of lactic acid *via* acetaldehyde, by Goldman and Yagoda[15] for the determination of traces of formaldehyde in the air and modified by us for the determination of acetaldehyde in dilute solutions.

This method depends on the fact that at a pH of about 2, (approximately that of a bisulphite solution), the dissociation constant of the aldehyde-bisulphite compound is a minimum while at a pH of 8, (the pH of a bicarbonate solution), the dissociation of the aldehyde addition compound is rapid. When the aldehyde solution was allowed to stand in the presence of excess sodium bisulphite until the reaction had gone to completion and the excess bisulphite then removed with iodine, the bound sulphite was released upon addition of sodium bicarbonate and titrated with dilute iodine. This gave a direct measure of the aldehyde in solution.

The results obtained with a series of standard solutions at different concentrations are given in Table I. These results were slightly better than those of Reynolds and Irwin[2] who claimed a 90 *per cent.* accuracy while the mean obtained in this investigation was 92·7 *per cent.* with a standard deviation of 1·5 *per cent.* Moreover this factor was constant for solutions containing from 0·2 to 0·5 g. acetaldehyde per litre. The method was therefore perfectly satisfactory for the determination of small quantities of the compound, provided the correction was applied.

The procedure has nevertheless two disadvantages: the titration was from colourless to blue which has been shown to be less satisfactory than the reverse[12], and considerable error could be introduced by oxidation of the sulphite released after the addition of the sodium bicarbonate by the air. These errors were, however, greatly minimised, if not totally eliminated, by the use of dilute solutions, titrating the bound bisulphite as soon as it was released and keeping the system at 0°.

TABLE I

Theoretical acetaldehyde conc.	Weight acetaldehyde found	Percentage found	Mean percentage found	Standard deviation	99 *per cent.* confidence limits
g./l.	g./l.				
0·500	0·466	93·2			
	0·470	94·0			
	0·466	93·2			
	0·459	91·9	93·3	0·9(7)	91·9-94·7%
	0·466	93·2			
	0·459	91·9			
	0·472	94·4			
	0·472	94·4			
0·400	0·364	91·0			
	0·371	92·7			
	0·362	90·5			
	0·370	92·5			
	0·371	92·7			
	0·373	93·2	91·2	1·2(9)	90·0-92·4%
	0·356	89·0			
	0·364	91·0			
	0·357	89·2			
	0·366	91·5			
	0·366	91·5			
	0·362	90·5			
0·300	0·282	94·0			
	0·283	94·3			
	0·280	93·3	93·0	2·5(2)	90·5-95·5%
	0·275	91·7			
	0·276	92·0			
	0·278	92·7			
0·200	0·188	94·0			
	0·189	94·5			
	0·190	95·0			
	0·189	94·5	94·0	1·0(5)	92·5-95·5%
	0·188	94·0			
	0·188	94·0			
	0·184	92·0			
	0·185	92·5			
		Total Mean	92·7	1·5	92·0-93·4%

EXPERIMENTAL

The solution (2·0 ml.) containing acetaldehyde was neutralised (if necessary) with 0·1 N sodium hydroxide (phenolphthalein). 25 *per cent.* Sodium bisulphite solution (20 ml.) was added and the mixture allowed to stand stoppered at room temperature for about 1½ hours before cooling in ice for 20 to 30 minutes. When the solution was thoroughly cooled, excess bisulphite was removed by the addition of iodine solution (20 g. iodine and 37 g. potassium iodide per litre), starch (1 ml.) added near the end point and the slight excess of the iodine immediately removed with 0·1 N sodium thiosulphate. The end point was adjusted to a faint blue with the aid of the dilute iodine solution so that the colour persisted for at least 30 seconds. The flask was then returned to the ice bath for 5 minutes and the bound bisulphite released by the addition of saturated sodium bicarbonate (15 ml.). Standard dilute iodide solution (approximately 0·008 N) was then run in at such a rate as to keep

pace with the decomposition of the addition compound. Near the end point 10 *per cent.* sodium carbonate solution (2 ml.) was added to ensure that the reaction had gone to completion.

Each experiment was carried out in triplicate, blank experiments being performed in every case. The standard solution of acetaldehyde was prepared by weighing out freshly distilled acetaldehyde (5 g.) in a weight burette and discharging the contents under water to eliminate losses due to evaporation. The solution was quickly made up to one litre and then further diluted to cover the range of concentrations required.

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SELF-DIFFUSION OF THE LOWER ALKYL IODIDES AND BROMIDES

by **L. H. STEIN and P. C. CARMAN**

OPSOMMING

Die kapillere buis metode is gebruik om die eie-diffusie koeffisiente van metiel jodide en etiel, *n*-propiel, *iso*-propiel, *n*-butiel, , *iso*-butyl en *sek*-butiel jodides en bromides te bepaal by drie verskillende temperature. Vir herkenning van die verbindinge is I^{131} en Br^{82} gebruik. Diffusie koeffisiënte was van die omvang van 2×10^{-5} cm.^{2}. sek.$^{-1}$ en aktiveerings energieë, 2 k kal./mole. Aktiveerings energieë val saam met die vir viskose stroming soos vereis deur die teorieë van Eyring en Frenkel. Die waardes van $D\eta/T$ was redelik konstant maar parameter-waardes afgelei van die vergeykinge van Eyring, Frenkel en Stokes-Einstein het swak ooreengestem met verwagte waardes. Toepassing van die eksperimentele bepalings dui aan dat die teorieë van Eyring en Frenkel slegs benaderinge is.

SUMMARY

Self-diffusion coefficients of methyl iodide and ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *iso*-butyl and *sec*-butyl iodides and bromides were determined at three temperatures by the capillary tube method using I^{131} and Br^{82} for labelling the compounds. Diffusion coefficients were of the order of 2×10^{-5} cm.^{2} sec.$^{-1}$ with activation energies of 2 kcal./mole. Activation energies agree with those for viscous flow as required by the theories of Eyring and Frenkel. The values of $D\eta/T$ were reasonably constant but parameter values calculated from the equations of Eyring, Frenkel and Stokes-Einstein were in poor agreement with experimental values. Application of experimental results indicated that the Eyring and Frenkel theories are only approximations.

In the studies of the liquid state, data on transport properties, namely, diffusion, viscosity and thermal conductivity are of great importance. Owing to its ease of measurement, much attention has been given to viscosity. Diffusion, however, is a property which is more clearly and simply related to thermal molecular motion. With an increasingly abundant supply of isotopes available, measurements of self-diffusion coefficients are now regularly carried out. In the case of liquids, self-diffusion coefficients of lead[1], mercury[2,3], water[4-13], benzene, ethyl bromide, ethyl alcohol[10], and other lower alkyl alcohols[11], sulphur[14], carbon disulphide[15], carbon tetrachloride[16], *n*-pentane and *n*-heptane[17], have been reported, many during the course of the present work. It was felt that a study of the lower alkyl halides would be of interest if precautions were taken to ensure accurate values. These materials can be readily labelled[18] with I^{131} and Br^{82} which have sufficiently useful half-lives of 8·06 days and 35·9 hours[19] respectively.

As data on viscosity of pure liquids are fairly extensive and where deficient can be readily supplemented, it was decided to consider both self-diffusion coefficients and viscosities of the liquids concerned in relation to existing theories.

EXPERIMENTAL

Materials. The compounds were purified by washing with sodium thiosulphate, drying with calcium chloride or potassium carbonate and fractionally distilling either at atmospheric or reduced pressure. Purity was ensured by checking the boiling points at the relative pressures and by refractive indices.

The radioactive isotopes obtained from England were converted to the lithium salts. Aliquots of suitable specific activity were used to label the alkyl halides by an exchange reaction carried out in a suitable solvent such as acetone, methyl ethyl ketone or ethylene glycol diacetate. By careful distillation the pure labelled compounds were obtained. Great care was necessary to ensure that there was no trace of colour in the liquids.

Diffusion measurement and apparatus. The capillary tube method of Anderson and Saddington[20], later modified by Wang[8], was employed with minor modifications to suit alkyl halides. The capillaries, closed at one end, were either 0·68 or 0·5 mm. in diameter and 2, 3, or 4 cm. in length. As depicted in *Fig.* 1, the diffusion cells consisted of a containing vessel and a domed upper part. The containing vessel was fitted with a B-29 socket and was about 3 cm. in diameter and 13 cm. high. The domed part which fitted into this was made from a B-29 cone and carried a centrally placed rod to which two cups were attached to carry two capillaries in a vertical position. Relative to the rod, a sleeve was offset in the dome and a stirrer passed through this and held in position by a rubber collar. The stirrer was a rectangle of glass which passed around the cups and stirring was achieved by vertical movement. The cell required 33 ml. of liquid to ensure good coverage of the capillaries.

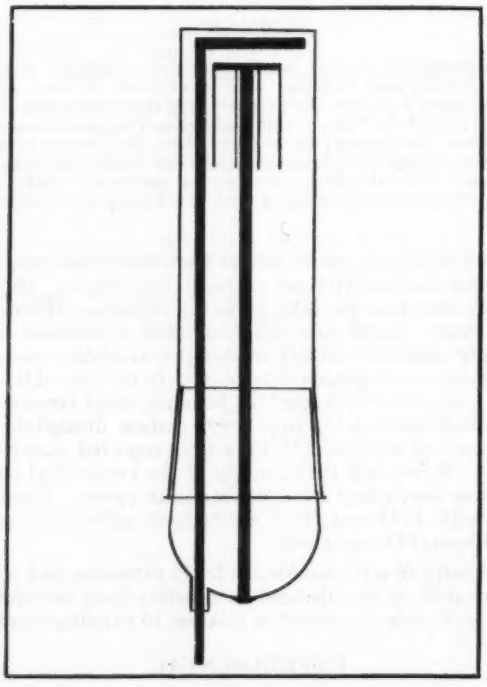

Fig. 1
Diffusion Cell

The diffusion coefficient was calculated from the equation derived[21] from Fick's Law, namely:

$$\frac{C_{Av}}{C_o}=\frac{8}{\pi^2}\sum_{n=o}^{n=\infty}\frac{1}{(2n+1)^2}\exp\left(\frac{-(2n+1)^2\pi^2Dt}{4l^2}\right)$$

where C_o and C_{Av} are the concentrations before and after diffusion, D is the diffusion coefficient in cm.^{2} sec.$^{-1}$, t is the time in seconds and l is the length of the diffusion path in cm. The above equation may be written in the form:

$$\frac{C_{Av}}{C_o}=\frac{8}{\pi^2}\ e^{-\theta}\left(1+\frac{e^{-8\theta}}{9}+\frac{e^{-24\theta}}{25}+\ldots\ldots\right)$$

where $\theta=\pi^2Dt/4l^2$. The bracketed terms were evaluated by successive approximation.

The capillary tubes were overfilled with active alkyl halide at the start of a run by means of a fine pipette fitted to a micrometer syringe. The liquid and the capillaries were at the same temperature as the liquid into which the capillaries were then carefully lowered. By slow rotation of the domed portion the liquid not in the capillary itself was displaced and a clearcut boundary established between the active and inactive materials. In the first hour slow stirring ensured that the concentration at the mouth of the tubes was zero with respect to active material and thereafter this condition, essential to the derivation of the above equations, was maintained by convection in the bulk liquid. After a suitable time the tubes were carefully removed from the cell, immersed in about 15 ml. of chloroform and the contents washed out with chloroform. The resulting solution was made up to a desired volume preparatory to counting. For obtaining the initial concentration the tubes were overfilled with active material at the desired temperature and the excess liquid allowed to evaporate. The tubes were immediately immersed in chloroform, the contents washed out and the solution made up for counting.

Solutions were counted in liquid counters, based on the design of Veall[22], used in conjunction with standard counting equipment. The necessary corrections for coincidence, background and decay were applied. The tops of the counters were ground flat and sealed with a glass plate lubricated with glycerine to obviate loss of volatile halides during counting.

Diffusion coefficients were measured at 7·35, 19·35 and 30·0°. These temperatures were maintained to within 0·03° in constant temperature water baths kept in constant temperature rooms adjusted near the experimental temperatures.

Viscosities were measured for those compounds for which the data in the literature were insufficient. An Ostwald type of viscometer, calibrated with water and benzene, was used to evaluate the viscosities at the temperatures cited above.

Effect of Time. The time t chosen for the evaluation of D is important as C_{Av} varies exponentially with time; the longer the time the smaller the errors in the determination of D. It was not practical, however, to choose long times as this would have incurred large losses in activity with corresponding counting difficulties and, in the case of the bromides, loss of opportunity for replication. It was found experimentally that for values of t such that $C_{Av}/C_o=0{\cdot}55$ or less, reasonable results could be obtained. This experiment also indicated that there was no marked change of D with time so that the effects of vibration and convection in the tubes could be neglected.

Length of the Diffusion Path. Since unsuitable stirring or convection in the cell could lead either to concentration of material at the mouth of the tube or to loss by

being swept out of the tube, thus altering the diffusion path length, experiments were carried out with tubes of differing length. No effects due to an altered diffusion path length were found under the experimental conditions chosen, even in the case of short tubes.

Tube Diameter. Throughout the investigation two sets of tubes of different diameters were used. For these tubes no differences were found unless stirring was excessive or the cells were subject to vibration. Where discrepancies were found between the two sets of tubes, the results were not used as these indicated that there had been loss of activity from the wider tubes owing to effects other than that of diffusion.

Hydrostatic Effect. Experiments using different levels of liquid in the cells indicated that within the limits chosen there was no hydrostatic effect.

All diffusion coefficients were measured several times. Because of the random nature of the decay process it was difficult to determine C_{Av} and C_o with a high degree of accuracy and the resultant values of D were liable to a degree of uncertainty which could only be overcome by repetition.

RESULTS

In Table I the values for the diffusion coefficients at the three temperatures listed are given together with standard deviations of the means for the number of replications indicated.

TABLE I

SELF-DIFFUSION COEFFICIENTS OF THE LOWER ALKYL IODIDES AND BROMIDES

Temp. °C.	Compound	$D \times 10^5$ cm.^{2} sec.$^{-1}$	Reps*	Compound	$D \times 10^5$ cm.^{2} sec.$^{-1}$	Reps*
7·35	MeI	2·166±·013	16			
19·35		2·671±·018	14			
30·00		3·241±·025	13			
7·35	EtI	1·838±·015	18	EtBr	2·847±·035	16
19·35		2·212±·014	32		3·483±·033	48
30·00		2·589±·013	29		4·176±·084	15
7·35	*n*PrI	1·362±·011	28	*n*PrBr	2·026±·009	31
19·35		1·623±·011	32		2·380±·014	39
30·00		1·922±·016	40		2·751±·014	31
7·35	*iso*PrI	1·435±·012	24	*iso*PrBr	2·077±·012	15
19·35		1·725±·008	20		2·467±·012	16
30·00		2·049±·011	20		2·893±·012	16
7·35	*n*BuI	1·135±·008	28	*n*BuBr	1·588±·008	16
19·35		1·347±·007	31		1·872±·011	16
30·00		1·685±·007	25		2·222±·011	16
7·35	*iso*BuI	1·044±·007	24	*iso*BuBr	1·495±·014	24
19·35		1·263±·007	23		1·800±·013	27
30·00		1·543±·007	28		2·170±·018	23
7·35	*sec*BuI	1·124±·006	32	*sec*BuBr	1·600±·013	16
19·35		1·353±·009	31		1·936±·011	19
30·00		1·607±·012	31		2·255±·022	20

*Reps=Replications.

The internal deviations were well below one *per cent.* in all cases except ethyl bromide which, like methyl iodide, was difficult to handle because of its low boiling point. The accuracy for ethyl bromide was, however, an improvement on that obtained by Graupner and Winter[10], who used a porous diaphragm method.

There was a definite decrease in D with increase in molecular weight for both series of compounds, which parallels the results obtained for the corresponding alcohols[11]. The *iso*-propyl halides both had distinctly higher self-diffusion coefficients than the corresponding normal compounds but in the butyl series the *iso*-compounds had lower coefficients than either the normal or secondary compounds which were similar in this respect.

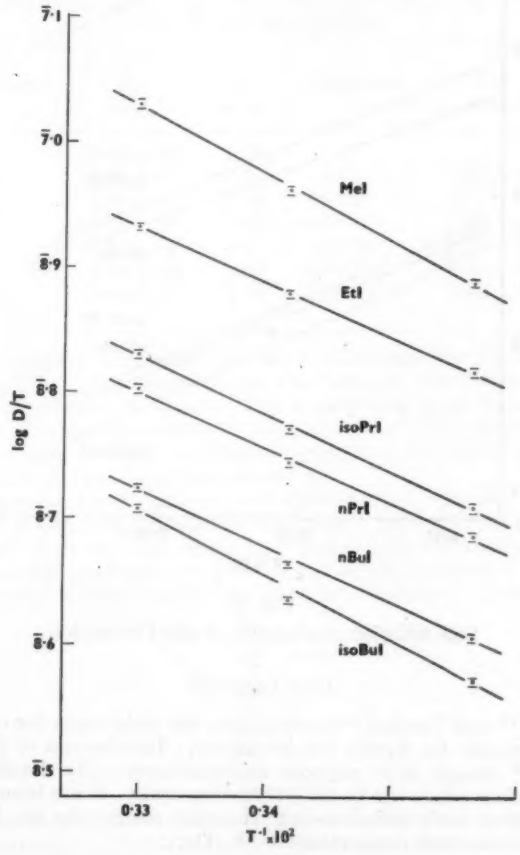

Fig. 2
Self-diffusion coefficients of alkyl iodides

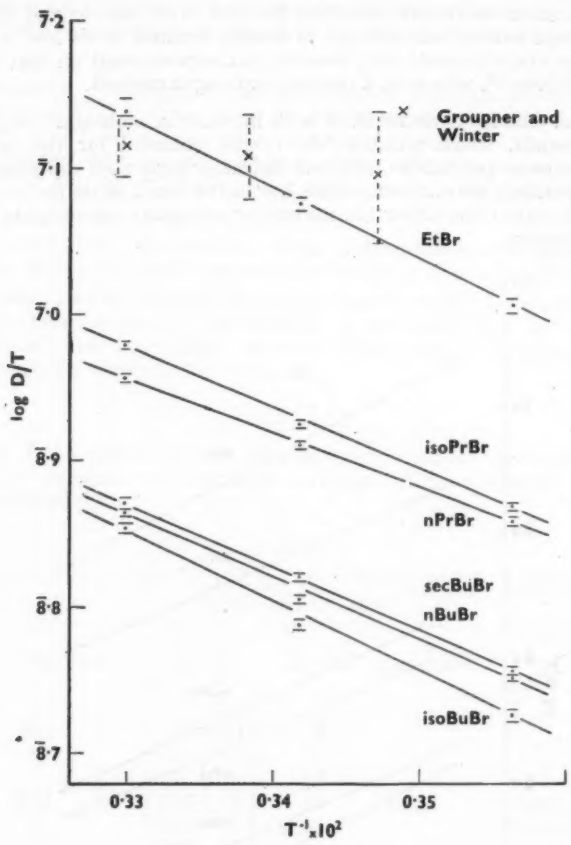

Fig. 3
Self-diffusion coefficients of alkyl bromides.

DISCUSSION

The Eyring[23] and Frenkel[24] theories give the only basis for calculation upon which diffusion results for liquids can be related. The theories of Born[25], Green[26] and Kirkwood[27] though more rigorous and mathematically detailed have not as yet led to expressions which can be tested experimentally. It has been well established experimentally that both diffusion and viscosity coefficients for liquids obey an exponential variation with temperature[28,29]. Thus:

$$D = D_o \exp.-E_D/RT$$
$$\text{and } \eta = \eta_o \exp. E\eta/RT$$

where η is the viscosity coefficient, D_o and η_o are the diffusion and viscosity constants and E_D and $E\eta$ the energies of activation. Plotting the log. of D or η against 1/T results in straight lines from the slopes of which the energies of activation can

be calculated. If, however, D_0 is temperature dependent and is proportional to T^n then, over the limited temperature range of a normal series of experiments, the plot of log. D *versus* 1/T gives a gradient corresponding to E_D+nRT. Since in general E_D is not many times greater than RT, the correction cannot be ignored. From the theories of Eyring and Frenkel $D\eta/T$ should be independent of temperature and as will be shown, this is borne out experimentally. In order therefore to obtain values of E_D relatively unaffected by temperature dependence of D_0, activation energy has been calculated from the plots of log. D/T versus 1/T for all the compounds as depicted in *Fig.* 2 and 3. The values obtained for E_D are compared with those for E_η from plots of log. η versus 1/T, in Table II.

TABLE II

VALUES FOR E_D AND E_η FOR THE LOWER ALKYL IODIDES AND BROMIDES

Compound	E_D kcal.	E_η kcal.	Compound	E_D kcal.	E_η kcal.
MeI	2·43±·10	1·58			
EtI	1·98±·10	1·52	EtBr	2·28±·14	1·90
*n*PrI	1·99±·12	2·20	*n*PrBr	1·71±·07	1·99
*iso*PrI	2·08±·10	1·96	*iso*PrBr	1·88±·09	1·84
*n*BuI	2·01±·09	1·95	*n*BuBr	1·93±·07	1·83
*iso*BuI	2·34±·08	1·95	*iso*BuBr	2·20±·14	1·98
*sec*BuI	2·09±·10	2·13	*sec*BuBr	1·99±·14	1·85

The E_D values in each series are similar although the values for the *iso*-compounds are slightly higher than those for their isomers. The lower boiling compounds have higher values than the others. This is surprising since the agreement found in the E_η values could be expected to be reflected in the values for the diffusion process. That the activation energies are similat throughout the series might be attributed to the predominant size of the halogen atoms.

The agreement for the processes of diffusion and viscosity is reasonably good and from this it can be expected that the values for $D\eta/T$ would be constant; this has been found to be the case, which is in accord with the theories of Eyring and of Frenkel. From the constants it is possible to calculate molecular parameters according to the Eyring, Frenkel and Stokes-Einstein equations. These are, respectively:

$$\frac{D\eta}{kT}=\frac{\lambda_1}{\lambda_2\lambda_3}$$

$$\frac{D\eta}{kT}=\frac{1}{\delta}$$

$$\text{and } \frac{D\eta}{kT}=\frac{1}{6\pi r}$$

where k is the Boltzmann constant, λ_1 is the distance between two parallel layers of moving molecules, λ_2 is the distance between molecules in the same layer at right angles to the direction of movement, λ_3 is the distance between molecules in the direction of movement, δ is the distance which a molecule moves in a single jump, and r is the radius of a molecule. In Table III calculated values for λ_1, $(\lambda_2\lambda_3)^{\frac{1}{2}}$ and $\lambda_2\lambda_3/\lambda_1$ are compared with values estimated from models[30]. In Frenkel's equation, no distinction is made between λ_1, λ_2, λ_3 and δ, so that $\lambda_2\lambda_3/\lambda_1$ corresponds to δ.

TABLE III

EYRING VALUES FOR λ_1, $(\lambda_2\lambda_3)^{\frac{1}{2}}$ AND $\lambda_2\lambda_3/\lambda_1$ Å

Compound	From exptl. Dη/T values λ_1	$(\lambda_2\lambda_3)^{\frac{1}{2}}$	$\lambda_2\lambda_3/\lambda_1$	Estimated from models λ_1	$(\lambda_2\lambda_3)^{\frac{1}{2}}$	$\lambda_2\lambda_3/\lambda_1$
MeI	1·83	7·58	31·3	3·50	4·27	5·28
EtI	2·08	8·02	31·3	3·50	5·41	8·40
*n*PrI	2·20	8·56	33·3	3·50	5·61	9·01
*iso*PrI	2·22	8·64	34·5	4·60	6·36	8·77
*n*BuI	2·34	8·99	34·5	3·50	6·03	10·42
*iso*BuI	2·30	9·10	35·7	4·83	6·65	9·17
*sec*BuI	2·28	9·15	37·0	5·21	6·46	8·00
EtBr	2·06	7·76	29·4	3·50	5·23	7·81
*n*PrBr	2·15	8·38	32·3	3·50	5·48	8·55
*iso*PrBr	2·14	8·51	33·3	4·60	6·19	8·33
*n*BuBr	2·27	8·85	34·5	3·50	5·96	10·10
*iso*BuBr	2·27	8·90	34·5	4·86	6·50	8·70
*sec*BuBr	2·29	8·87	34·5	5·00	6·26	7·87

The agreement is not good and even the ratios $\lambda_2\lambda_3/\lambda_1$ are not comparable. Furthermore, values indicate that the Frenkel value is only a very rough approximation. The product $\lambda_2\lambda_3$ appears to increase fairly regularly, however, and if the lateral distance between chains is nearly constant in each series this product would be approximately proportional to the lengths of the molecules. The fact that λ_1 is the smallest value bears out the Eyring definition for this parameter for non-spherical molecules, but the values are smaller than the diameters of the halogens concerned.

In Table IV a comparison is made of the values obtained from the Stokes-Einstein equation with values of $\frac{1}{2}(V/N)^{\frac{1}{3}}$, where V/N is the molecular volume. The maximum radii are also included for both the stretched and coiled configurations of the molecules.

TABLE IV

STOKES-EINSTEIN VALUES OF MOLECULAR RADII Å

Compound	From exptl. Dη/T values	$\frac{1}{2}(V/N)^{\frac{1}{3}}$	Estimated from models $r_{stretched}$	r_{coiled}
MeI	1·64	2·35	2·64	2·64
EtI	1·64	2·55	3·33	3·14
*n*PrI	1·77	2·72	3·93	3·33
*iso*PrI	1·79	2·75	3·32	3·15
*n*BuI	1·83	2·87	4·54	3·25
*iso*BuI	1·91	2·88	3·93	3·35
*sec*BuI	1·95	2·88	3·70	3·30
EtBr	1·55	2,50	3·60	3·01
*n*PrBr	1·73	2·66	3·25	3·18
*iso*PrBr	1·78	2·69	3·19	3·02
*n*BuBr	1·83	2·82	4·44	3·25
*iso*BuBr	1·85	2·82	3·75	3·18
*sec*BuBr	1·82	2·83	3·70	3·30

The values of r, though smaller, are more realistic than those given in Table III although the Stokes-Einstein equation is not expected to apply to the case of self-diffusion.

Eyring has developed the equation for diffusion:

$$D=\delta^2\frac{kT}{h}\frac{Q_{\ddagger}}{Q}\,e^{-\epsilon/kT}$$

where δ is the distance of jump of the molecule, h is Plank's constant, and $Q_{\ddagger}$ and Q are the partition coefficients in the activated and initial states for unit volume, respectively. On a quasi-thermodynamical basis he shows that:

$$D=\delta^2\frac{kT}{h}e^{-\Delta G^{\ddagger}/RT}$$

$$\text{and } D=\delta^2\frac{kT}{h}e^{\Delta S^{\ddagger}/T}\,e^{-\Delta H^{\ddagger}/RT}$$

where $\Delta G^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ are the free energy, entropy change and heat of activation respectively. Since diffusion is accompanied by negligible volume change[31], $\Delta H^{\ddagger}=\Delta E^{\ddagger}$, where $\Delta E^{\ddagger}$ is the internal energy of activation. If E'_D is the experimental energy of activation obtained by plotting log. D versus 1/T, and $\Delta S^{\ddagger}$ is independent of temperature, then $\Delta E^{\ddagger}=E'_D-RT$. As values of E_D have been obtained by plotting log. D/T versus 1/T, $\Delta E^{\ddagger}=E_D$.

Assuming as Eyring does that $\delta=(V/N)^{\frac{1}{3}}$, values of $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$ have been calculated and are given in Table V.

TABLE V

VALUES OF $\Delta G^{\ddagger}$ AND $\Delta S^{\ddagger}$ FOR THE LOWER ALKYL HALIDES

Compound	$\Delta G^{\ddagger}$ kcal./mole	$\Delta S^{\ddagger}$ E U	Compound	$\Delta G^{\ddagger}$ kcal./mole	$\Delta S^{\ddagger}$ E U
MeI	3·61	–4·02			
EtI	3·82	–6·32	EtBr	3·53	–4·28
nPrI	4·08	–7·10	*n*PrBr	3·83	–7·27
*iso*PrI	4·05	–6·71	*iso*PrBr	3·82	–6·56
*n*BuI	4·11	–7·22	*n*BuBr	4·03	–7·22
*iso*BuI	4·29	–6·69	*iso*BuBr	4·06	–6·35
*sec*BuI	4·25	–7·41	*sec*BuBr	4·02	–7·27

As found by Partington *et al.*[11] for the homologous series of alcohols, there is a small but steady increase in $\Delta G^{\ddagger}$ in spite of there being no trend in the variation of E_D. Contrary to their findings, however, the variation in $\Delta S^{\ddagger}$ is not haphazard but decreases with increasing molecular weight. The values for the iso-butyl compounds in each series resemble those of the *iso*propyl compounds and are of interest when one considers the fact that these compounds have 3-carbon chains with substituents on C_2.

The values of $\Delta S^{\ddagger}$ are negative and this might imply some degree of ordering or loss of rotation of the molecules. The values cannot, however, be taken as quantitative as they are very dependent on the value chosen for δ. It is of interest to note that for the similar process of viscous flow, Bondi[32] also found that values for $\Delta S^{\ddagger}$ were negative for the lower molecular weight hydrocarbons.

In Table VI values of D_o at 19·35°C calculated from D at this temperature and E_D in Table II are given. The theoretical values of D_o calculated from Eyring's equation are also given. These have been evaluated by the procedure of Graupner and Winter, according to which:

$$D_o=(V/N)^{\frac{1}{3}}\left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}}\left\{\frac{RT}{NP_v}\,e^{-(E_{vap}+RT)/RT}\right\}^{-\frac{1}{3}}$$

where m is the weight of a molecule of the compound, P_v the vapour pressure and E_{vap} the latent heat of vaporisation. Values for E_{vap} were calculated on the basis of the Hildebrand equation[33] as the values in the literature were varied and incomplete.

From the Frenkel equation:

$$D=\frac{\delta^2}{6\tau_o}\,e^{-E_D/RT}$$

$$\text{whence } D_o=\frac{\delta^2}{6\tau_o}.$$

Values of D_o at 19·35° calculated by assuming $\delta=(V/N)^{\frac{1}{3}}$ and taking for τ_o, the period of free vibration of a molecule, the time taken to travel distance δ at the average thermal velocity $\left(\frac{8kT}{\pi m}\right)^{\frac{1}{2}}$, are included in Table VI.

TABLE VI

EXPERIMENTALLY DERIVED AND CALCULATED VALUES OF D_o AT 19·35°.

Compound	D_o Exptl.	D_o Eyring	D_o Frenkel	Compound	D_o Exptl.	D_o Eyring	D_o Frenkel
MeI	17·49	14·2	1·63				
EtI	6·68	16·5	1·70	EtBr	17·62	18·4	1·99
*n*PrI	4·98	18·8	1·73	*n*PrBr	4·51	20·5	1·99
*iso*PrI	7·78	18·9	1·75	*iso*PrBr	6·27	20·8	2·01
*n*BuI	4·28	20·7	1·76	*n*BuBr	5·18	22·6	2·00
*iso*BuI	7·08	20·5	1·76	*iso*BuBr	7·93	22·5	2·00
*sec*BuI	4·93	20·7	1·76	*sec*BuBr	5·94	22·6	2·00

The Frenkel value can only be expected to be a rough estimate and this appears to be the case. The Eyring equation is supposed to give a better estimate but does not give very good values compared with those derived experimentally. Graupner and Winter[10] found a similar lack of agreement.

Apart, therefore, from the similarity of the energies of activation for the diffusion and viscous flow processes and the resulting constancy of $D\eta/T$, these theories appear to give only approximate values and do not offer a reliable approach to the understanding of the mechanism of liquid diffusion.

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THE DETERMINATION OF NITRATE IN THE PRESENCE OF NITRITE IN DILUTE AQUEOUS SOLUTION

by **E. G. WHITE and K. A. MURRAY**

OPSOMMING

Dit is ons mening dat die geskikste vinnige roetinemetode om nitrate in wateroplossings (bv. rioolslykwaters) te bepaal, die kolorimetriese fenolsulfoonsuur metode is. Nitriete, wat hierdie metode affekteer, kannie maklik sonder die verlies van nitrate vernietig word nie; besware teen die verskeie chemiese metodes om nitriete tot nitrate te oksideer, word gemaak. Daar is gevind dat 'n elektrolitiese oksidasiemetode, waarin 'n lae stroomdigtheid gebruik word, bevredigend is en dit vorm dan ook die basis van die nuwe metode. Die nitriet konsentrasie is eers volgens die Griess-Ilosvay metode bepaal. Die nitriete is dan elektrolities tot die nitrate geoksideer en die totale nitraatkonsentrasie dan volgens die fenolsulfoonsuurmetode bepaal.

SUMMARY

It is considered that the most suitable rapid routine method for determining nitrate in aqueous solution (e.g. sewage effluent) is a colorimetric one using phenolsulphonic acid. In this method nitrite interferes and cannot readily be destroyed without the loss of nitrate; objections to the various chemical methods of oxidizing nitrites to nitrates are given. An electrolytic oxidation method using low current densities has been found to be satisfactory and this forms the basis of a new method. Nitrite is determined by the Griess-Ilosvay method and nitrite, in a separate portion, is then oxidized electrolytically to nitrate which is determined by the phenoldisulphonic acid method.

Phenoldisulphonic acid method. Sprengel[1] discovered the reaction of nitrate with phenoldisulphonic acid and the basis of the present procedure with this reagent was established in 1885 by Granval and Lajoux[2]. Chamot and Pratt[3,4], later assisted by Redfield[5,6] investigated this reaction fully, showing that the yellow colour produced is due to the formation of the alkali salt of nitrophenoldisulphonic acid. They further worked out a reliable method of preparing the reagent and studied precautions necessary in carrying out an analysis.

Chloride has a marked and irregular interfering effect on the phenoldisulphonic acid method of Chamot and Pratt, shown by Farey[7] to be due to the loss of nitrate as volatile nitrosyl chloride which, however, is unstable in the presence of water. Frederick[8] modified the method so that nitration took place in the presence of water, thus reducing the interference by chloride to some extent.

Nitrite also interferes in the phenoldisulphonic acid method. Tatlock and Thomson[9] indicated that nitrite only slightly raised the proportion of nitrate. However, this is not so when nitrite is in excess of one part per million (as nitrogen) and Chamot *et al.*[6] recommended oxidation of nitrite by hydrogen peroxide or permanganate before determining nitrate.

Other colorimetric methods. Many substances in concentrated sulphuric acid solution give brilliantly coloured compounds in the presence of nitrate, and some of them have been adapted to estimating nitrate colorimetrically. Nitrite usually interferes, as well as certain oxidizing agents.[10,11,12]

Buckett, Duffield and Milton[13] destroy nitrite by means of urea in weakly acid solution, which does not affect nitrate, and then determine the nitrate with 2:4

—xylenol, using the method suggested by Barnes[14]. This method avoids steam distillation but involves a double extraction with toluene and subsequent extraction of the toluene with sodium hydroxide. The authors[13] state that the degree of nitration of 2:4—xylenol by nitrates in the presence of sulphuric acid is not quantitative and that conditions must be carefully controlled to make results reproducible. This added to the tendency of the toluene-sodium hydroxide mixture to form an emulsion, makes the method unsuitable for rapid routine analyses. (Destruction of nitrite by means of urea is undesirable in the phenoldisulphonic acid method as urea in the presence of the strong acid will also destroy nitrate. It would be necessary to complicate the method by removal of all excess urea before adding the phenoldisulphonic acid).

Reduction methods. Of the various methods of reducing nitrates and nitrites to ammonia, that using Devarda's alloy has much to commend it. Devarda's[15] original method has been modified by Donald[16] and more recently by Allerton[17], who adapted the method for small amounts of nitrate in water. Other reducing agents have also been tried, such as ferrous sulphate with various catalysts[18,19,20], and titanous salts[21]. These methods all require the separate determination of both ammonia and nitrite. According to the American Public Health Association's "Standard methods"[22] the reduction method is not very accurate on account of the hydrolysis of some organic nitrogen as well as possible loss of nitrogen due to incomplete reduction of the nitrate or incomplete recovery of the ammonia.

Nitrite can be accurately determined by the Griess-Ilosvay method[22,23]; nitrate does not interfere.

EXPERIMENTAL

Electrolytic oxidation of nitrite. In initial attempts to oxidize nitrite electrolytically it was noted that with low current densities nitrate formed at the anode and ammonia at the cathode. The solution at the anode was therefore separated from that at the cathode by a porous clay pot inside a beaker. The porous pot and beaker were filled to the same level with a dilute solution of sodium nitrite. Electrodes of bright platinum sheet, 1 sq. in. in area, were used, the anode being placed in the porous pot. A current of 0·1 amp. at 30v. between the electrodes caused oxidation of nitrite in the anolyte and reduction in the catholyte, with some heating. At the same time pronounced electro-osmosis took place, a considerable volume of water in the anolyte passing through to the catholyte.

In solutions of low sodium nitrite concentration (e.g. 20 parts per million of nitrite nitrogen) insufficient current passed between the electrodes. Sulphuric acid at a concentration of 0·2 *per cent.*, which did not cause loss of nitrite, increased the conductivity sufficiently to allow the passage of 0·3 amp. at 30 v. but heating and electro-osmosis still occurred. A potential of 12 v. allowed the passage of less than 0·2 amp. and avoided undue heating of the solutions. However, electro-osmosis was marked as also when other substances (e.g. sodium hydroxide, sodium sulphate, sodium carbonate, potassium bisulphate) were used to increase conductivity.

A 50 ml. pyrex sintered glass disc crucible, porosity 4 with the bottom end of the cylindrical wall ground flush with the lower face of the sintered glass disc(to avoid entrapping gas bubbles) was then used in place of the porous pot; this prevented electro-osmosis. Using this crucible and sodium nitrite (20 p.p.m. nitrite nitrogen) in 0·2 *per cent.* sulphuric acid, oxidation in the anode compartment and reduction in the cathode compartment were carried out for 1 hour at 12 v.

During this period the current fell from 0·3 amp. to a final value of 0·14 amp. The height of the crucible in the beaker was so adjusted that on pouring 35 ml.

nitrite solution into both the crucible and the beaker the resultant levels were the same.

The following results were obtained:

	Nitrite N	Nitrate N	Ammon. N
Original solution	20	Nil	Nil
Final anode solution	Nil	20	Nil
Final cathode solution	Trace	Nil	19

Nitrite nitrogen was determined by the Griess-Ilosvay[22] method, nitrate nitrogen by the phenoldisulphonic acid method or by reduction to ammonia, and ammonia nitrogen with Nessler's reagent, comparisons being made in an 'Eel' absorptiometer.

In further experiments nitrites were readily oxidized to nitrates at the anode when sulphuric acid, sodium hydroxide, sodium sulphate, or other electrolytes were added to increase conductivity. Chloride was avoided because of its subsequent interference in the phenoldisulphonic acid method.

Electrolysis of sewage effluent. Analysis of the anolyte and catholyte before and after electrolysis indicated that in a solution such as sewage effluent containing ammonia, nitrite and nitrate the following took place:

> Ammonium ions migrated to the cathode, nitrate ions to the anode and nitrite ions in sulphuric acid solution remained at the cathode where they were completely reduced to ammonia except when in high concentration (greater than 20 p.p.m. nitrogen), in which case migration to the anode occurred to some extent. In alkaline or neutral solution (which soon became alkaline at the cathode), a portion of the nitrite tended to migrate to the anode.

Under these conditions nitrate was not reduced at the cathode or ammonia oxidized at the anode. Ammonia does not therefore interfere with oxidation of nitrite nor in the subsequent determination of the resulting nitrate.

An incompletely oxidized sewage effluent was electrolysed at 12 v. and 0·15 amp. for 1 hour, sulphuric acid having been added to give a 0·1 *per cent.* solution. The current decreased to 0·05 amp. at the end. 35 ml. Solution was placed in each compartment. The following results were obtained:

	Nitrite N	Nitrate N	Ammon. N
Original solution	5·1	11·0	0·7
Final solution at anode ..	Nil	25·0	0·2
Final solution at cathode ..	Nil	2·1	6·2

The nitrite at the anode was oxidized to nitrate and most of the nitrate in the catholyte migrated to the anode; further, nitrite at the cathode was reduced to ammonia and most of the ammonia originally in the anolyte migrated to the cathode. On passing the current for a longer period, all the nitrate appeared at the anode and all the ammonia at the cathode.

Because of the migration of the ions as described, electrolysis was repeated with sewage effluent as anolyte and distilled water containing 0·1 *per cent.* sulphuric acid in the cathode chamber. The following results were obtained after 1 hour's electrolysis:

	Nitrite N	Nitrate N	Ammon. N
ANODE: Original solution ..	5·1	11·0	0·7
Final solution.. ..	Nil	16·0	0·2
CATHODE: Original solution ..	Nil	Nil	Nil
Final solution ..	Nil	Nil	0·5

DISCUSSION

Irregular interference of nitrite in the phenoldisulphonic acid method is shown by the following results obtained with an 'Eel' absorptiometer:

Nitrite nitrogen p.p.m.	Apparent nitrate nitrogen
10	2
10	3
20	5
20	4
30	11
30	9

Oxidation by hydrogen peroxide or permanganate as recommended by Chamot *et al.*[6] is not satisfactory in ordinary routine analysis. In the modified phenoldisulphonic acid method of Frederick[8] nitrite causes less interference than in the normal method, but interference is irregular especially if heating is prolonged. Eastoe and Pollard[24] have suggested a modified phenoldisulphonic acid method where nitration is carried out in the presence of water. They claim that in comparison with the standard method nitrite is determined quantitatively by the modified procedure as if it were nitrate. Also, they aver that nitrite does not affect the standard method. This latter statement is in conflict with the figures we have given and with the effect of nitrite previously recognised by others.[6, 11]

We are unable to substantiate the statement of Eastoe and Pollard[24] in view of the following results:

Sodium nitrite solution	N found as nitrate	
p.p.m. of N	Method of Eastoe and Pollard[24]	Authors' method
1	0·5	1
3	1·2	3
4	1·6	
5	1·8	5
6	2·4	
8	3·0	8
10	4·0	10
15	7·0	15
20	11·0	20

Solutions of A.R. sodium nitrite were used; determinations were made on an 'Eel' absorptiometer.

The accuracy of our method was confirmed by twelve analysts who reported a mean result of 30·0 p.p.m. of nitrite nitrogen (theoretical 30·0 p.p.m.) standard deviation 0·24, after electrolysis of a solution containing initially nitrate (20 p.p.m. N), nitrite (10 p.p.m. N) and ammonium ions (10 p.p.m. N).

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